University of Sheffield | Energy Innovation Centre

Investigating the Impact of Reducing the Aromatic Content of Kerosene

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Disclaimer

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Foreword

Aviation plays a vital role in our global transportation system, connecting people and goods across continents. However, technologies that could decarbonise aviation such as electrification or hydrogen are at an early stage of development and therefore the use of liquid hydrocarbon fuels (kerosene – regardless of source, fossil-based, sustainable, or synthetic) is the only option for the foreseeable future, particularly for long haul flight using the existing hardware and supply infrastructure. Beyond the well-known carbon dioxide (CO_2) emissions associated with burning jet fuel, there are other environmental consequences that warrant attention. One such aspect is the presence of aromatic compounds in aviation fuel.

The objective of this report is to provide an in-depth critical review of the interaction between the chemical components of jet fuel (kerosene) and contrail formation, and the impacts on radiative forcing and climate. Fossil fuel-based jet fuels will remain the predominant fuel used by the aviation industry for several years until sustainable aviation fuels (SAF) and zero-emission fuel industries develop at scale. Previous detailed studies have identified the impact of the aromatic content of kerosene on non-CO_2 emissions and the formation of contrails, therefore, it is important to understand the magnitude of their impact and explore the available mitigation options.

This report gathers and performs analyses regarding the reduction and/or removal of the aromatic content of kerosene to mitigate contrail formation. It addresses technical challenges related to engine performance, safety considerations, cost implications, and any potential CO_2 trade-offs. Additionally, the report sheds light on how different fuel components, such as aromatics, sulphur, and naphthalene, can influence pollutant emissions.

The report initially examines refinery processes to reduce and/or remove aromatics and naphthalene from jet fuel. It evaluates the resources required at the refinery and the economic costs associated with the desired range of fuel compositions. Additionally, the report focuses on understanding how the resulting changes in fuel composition may be brought about by specification controls and the subsequent impact on engine performance, non-CO_2 emissions, and the possibility of relationships between particulate matter emissions and fuel composition. Finally, the report provides key findings, highlighting knowledge gaps and recommendations for future research.

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Executive summary

High level objective of this work

The primary objective of the work reported here was to explore the relationship between the aromatic content of jet fuel and contrail formation, and to establish if reducing the aromatic content of kerosene would have a positive climate impact. The analysis undertaken sought to identify the cost, safety, and operational implications of reducing the aromatic content of jet fuel to different levels and clarify the trade-offs between any extra CO_2 emissions generated during the hydrotreating process and the potential for reducing climate warming contrails.

Background

Aviation has several effects on climate through its CO_2 and non-CO_2 emissions. Emissions of CO_2 and its effects are well quantified and understood, and there are a variety of initiatives in place through international policy to address these emissions through technological (e.g. the International Civil Aviation Organization's CO_2 emissions standard) and market-based measures (e.g. the UK Emissions Trading Scheme for aviation and ICAO's Carbon Offsetting and Reduction Scheme for International Aviation [CORSIA]). There are also a number of initiatives in place to develop zero and low carbon fuel production technologies including 'Sustainable Aviation Fuels' (SAF), where the aim is to produce a fuel that has lower greenhouse gas emission 'footprint' (i.e. 'lifecycle' emissions) than fossil-derived Jet A/A-1. Such initiatives and ambitions for SAF are being supported by government and industry, e.g. in the UK through the Jet Zero Taskforce and the industry body 'Sustainable Aviation'. The UK government introduced a SAF mandate on the 1st of January 2025, which requires 2% of SAF in the UK's aviation fuel mix in 2025, increasing to 10% in

2030 and 22% in 2040 [Chapter 1]. In addition, government is supporting the advancement of other measures to aid decarbonisation of the sector including the development of hydrogen and electric powered flight.

The UK Government also recognises that aviation also has non-CO_2 impacts which could have a significant warming impact on the climate. In October 2023, the Department for Transport (DfT) alongside the Natural Environment Research Council (NERC) and Department for Business and Trade (DBT) in partnership with the Aerospace Technology Institute (ATI), launched a multi-year non-CO_2 research programme to better the understanding of aviation's non-CO_2 impacts and to identify and develop potential mitigation options. Calls for academic and industry projects took place in 2023 with ten academic projects then awarded funding by NERC in 2024. Further calls for both academic and industry projects will take place over the course of the programme's lifespan.

Of aviation's non-CO_2 effects, condensation trails – 'contrails' – are of significant interest, since they have been quantified to currently contribute the largest effect of aviation on climate (in terms of the scientific metric of quantification widely used – 'radiative forcing' – in watts per square metre) and are largest among aviation's 'non-CO_2' effects. [Chapter 6]

Contrails are line-shaped ice crystal clouds that are formed behind aircraft at cruising altitudes (approximately 8 – 12 km). For the current aircraft fleet, they are principally formed from water vapour in the exhaust condensing on soot particles (the product of incomplete combustion), which rapidly freeze, and take up further water vapour from the background atmosphere under specific conditions of humidity and cold temperatures. These line-shaped contrails may spread, under 'ice supersaturated' conditions of cold atmospheres, to form large decks of cirrus-like clouds, occasionally extending 100s of km, disrupting the radiation balance of the atmosphere. Overall, these contrail-cirrus clouds are thought to warm the atmosphere through complex processes that have a number of dependencies on emissions and background conditions, and the effects are only quantified with large uncertainties (an estimated effective radiative forcing for 2018 of 57 mW m^{-2}, range 17 - 98 mW m^{-2}). [Chapters 1, 6]

The 'aromatic content' of jet fuel refers to certain organic chemicals naturally present in aviation fossil-based jet fuel (Jet A/A-1) [Chapter 2]. Aromatic compounds are unsaturated cyclic compounds with alternating single and double bonds between carbon atoms. Aromatics are some of the most complex components in Jet A/A-1 fuel and are less easily completely combusted than other 'bulk' components of the fuel. Nonetheless, their presence has benefits, in having a high molecular density, and they help sealing of fuel systems in aircraft by causing elastomeric seals to swell. The content of aromatic compounds is a part of the Jet A/A-1 fuel specification, which airframes and engines are certified to use. The specification has a maximum/minimum limit of <25%/8% (by volume) for total aromatics, and a maximum limit of <3% for the di-aromatic (or naphthalene) content (compounds with two rings), by volume. On average, Jet A/A-1 has around 16% total aromatics. There is no minimum aromatic limit for fossil fuels however, blends of fossil fuels and synthetic blend components are restricted to a minimum aromatic content of 8%. [Chapters 2, 3, 4] Aromatic compounds are of interest in relation to contrails and their effect on climate, since di- aromatics in particular, have been shown from measurements to be mostly (but not solely) responsible for producing soot particles in aircraft exhaust. [Chapter 5]

Thus, it has been suggested that removal of aromatic compounds from conventional fossil-based jet fuel may have environmental benefits in terms of reducing contrails, and their warming effect on climate.

Approach

The primary approach taken in the preparation of this report was to undertake a critical review of the literature and assess the potential impact of reducing aromatics in jet fuels on contrail formation and their effect on climate. The evidence base for the effect of contrails was assessed, along with the presence, properties, potential, and consequences for aromatic compound reduction.

The comprehensive literature review has highlighted gaps in our understanding of fuel chemical composition's impact on soot and ice crystal formation. Closing these knowledge gaps are crucial for addressing non-CO_2 emissions and understanding how jet fuel composition influences soot particle formation [Chapter 7]. To address this, primary data was gathered through a comprehensive emissions test campaign to provide in-depth information in relevant dimensions. The University of Sheffield's Energy Innovation Centre conducted tests on gaseous and particulate emissions from jet fuel with varying aromatic content. Five fuel samples were used, with aromatic content ranging from 0% to 15.6%. Additionally, fuel chemical analysis included assessing naphthalene content and the H/C ratio. [Chapter 5]

The influence of aromatic concentration in jet fuels on non-volatile particulate matter (nvPM) emission characteristics and NOx emissions during an APU ground test was investigated. The findings confirm that using conventional jet fuels with lower aromatic content could be an additional viable approach to mitigate aviation PM emissions while also improving energy density of the fuel with no significant impact on NOx emissions.

Findings

We find that the literature shows that the complete removal of di-aromatics from jet fuel could reduce soot (which plays an important role in contrail formation) by up to a factor of ten[1]. However, the detailed processes involved in soot formation in aircraft combustors are still poorly understood. [Chapter 5]

By adopting innovative refining technologies and minimising specific aromatic compounds in jet fuels, it is possible to significantly reduce aircraft emissions of soot particles. There is good evidence that soot emissions from fossil-based aviation kerosene play an important role in the formation of contrails. However, there is less confidence in the quantitative reduction of the radiative forcing effect as a result of minimising the aromatic content of the fuel and a consequent reduction in contrail formation. This is because the radiative effect can only be modelled and is some steps 'downstream' of quantified emissions. The evidence that soot is reduced (but not completely removed) by removal of di-aromatics from jet fuel is empirical, i.e. there is an incomplete understanding of theoretical processes leading to soot formation in an aircraft combustor.

Despite the potential for reducing soot and contrail formation through the removal of di- aromatics from jet fuel, we find that the effect of contrails on climate remains poorly quantified with large uncertainties. [Chapter 6]

The processes involved in contrail formation are complex, as are the quantification methods of their radiative effects. This has only been assessed with two current models, worldwide, that incorporate the

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[1] *It should be noted that changes in combustion technology from rich burn to lean burn engines may reduce soot emissions by orders of magnitude (per unit fuel burnt): however, any resultant effect on contrails has not been quantified and carries further uncertainties in terms of the emergent role of volatile particles already present in the exhaust, over the reduced soot particles.*

necessary water and cloud feedbacks. The results from these models cannot be described as 'stable', and the uncertainties are large and changing with new physical processes still being incorporated into the global modelling and new developments in understanding. The relative magnitude of the contrail effect is entirely dependent on the recent growth rate of aviation and is subject to change. Moreover, contrails are not the only effect of soot emissions from aircraft; the 'aerosol cloud interaction' has no best estimate quantified from the scientific literature but could be a negative forcing (implying cooling), which could be larger than the positive forcing of contrails. [Chapter 6]

We find that reducing the aromatic content of jet fuel will require more processing of the fuel at the refinery, and result in increased demand in energy and CO_2 emissions, so a trade-off situation will occur between potentially reduced contrails but increased CO_2 emissions (albeit out of sector). [Chapters 3, 6]

Two studies are available that indicate that increased energy requirements at the refinery may increase emissions of CO_2 by approximately 3% (97 kg CO_2/tonne of fuel). Given the lifetime of CO_2, this is significant. The 'CO_2-equivalents' (CO_2e) values of contrails carry significant uncertainties and subjective user choices (the CO_2e metric chosen and time horizon over which the calculation is made), which mean that the mean value (excluding uncertainties) can vary by a factor of approximately 20. At best, with a CO_2-e trade-off situation, a limited improvement can be realised: at worst, the environmental outcome is worsened as a result of targeting contrails, and the perspective on this relates to timescales (short- vs long-term). This has not been studied for this trade-off case. [Chapter 6]

We find that limiting aromatics will increase the costs of fuel production due to increasing the severity of the hydrotreatment process. [Chapter 4]

There are limited studies covering costs of production in literature, which are modelling studies of production and pilot scale hydroprocessing at various levels of single fuels. The studies which consider the combination of effects on fuel properties are even more limited and is an area for further research. The cost of increasing levels of hydrotreatment appears from the limited literature to be non-linear – complex molecules are first broken down into simpler hydrocarbon structures, preferentially removing tri- and di-aromatic components. More severe hydrotreatment is required to remove mono aromatics and is significantly more expensive (both in terms of cost, energy and the requirement for hydrogen).

This needs to be explored in the context of typical UK refineries and any additional hydrotreatment plant required for them to achieve a range of aromatic targets, from a naphthalene (a di-aromatic) only ceiling to a more energy intensive reduction in total aromatic limit. On average Jet A/A-1 has around 16% total aromatics, which includes both single ring and naphthalenes. These di-aromatics are known to produce higher levels of soot. Individual studies conclude that the complete removal of di-aromatics could reduce soot by up to a factor of ten. Limited research suggests removal of di-aromatics using hydrotreatment would increase the cost of aviation fuel by +4.7 US cents/Litre and +3.35g CO_2e/MJ in production. The impact of this increase on specific flights will depend on the volume of fuel required.

Moreover, conventional Jet A/A-1 aviation fuel is produced and sold as a commodity on a global market, produced from crude oil by refiners. Refineries are driven by techno- economics based on crude input and a wide range of output products of which jet fuel typically represents only 4%.

We note that with any changes in fuel there could be safety, operational and cost implications, which include the ground handling of fuel, and engine performance, maintenance and engine longevity. [Chapter 4]

The balance of changes in engine life due to increases in thermal stability and reduction in lubricity need to be investigated more systematically. There may be an increasing requirement for additives in the fuel;

specifically, lubricity enhancers and antioxidants, as the level of hydrotreating increases which will increase the cost of the fuel production further still. It is vital to ensure that engines are compatible with lower aromatic content without risking seal leaks. According to present understanding, reducing the aromatic content to 8% would not present any challenge to the seals or other elastomeric components. It would, however, create a fuel that could not be blended with a synthetic blending product, including SAF as further lowering of the aromatic content below 8% through blending would produce a fuel which would no longer be compliant with the Jet A/A-1 fuel specifications as a drop-in fuel.

We note that any increased requirement for hydrotreating will require increases in hydrogen demand for fuel production. Whilst the availability of green hydrogen remains constrained, this increased demand for hydrogen may conflict with the demand for hydrogen for the production of SAF, SAF derived from biomass and PtL SAF and for use in hydrogen-powered aircraft. [Chapter 3]

Changes in the aromatic and di-aromatic content limits of the fuel specification would require a substantial investment at the refinery, primarily around a more intensive hydrotreatment capability and increases in the consumption of hydrogen in producing jet fuel. However, doing so would bring about a risk to the more general availability of SAF which also requires hydrogen for production. Increased pull on hydrogenation capacity and consumption of sustainable hydrogen would be in direct competition with the production of SAF and for use in hydrogen-powered aircraft.

In order to understand this competition, more analysis is required to determine the technical, economic and environmental cost of the hydrotreating process (including increased maintenance due to reduced catalyst life as a result of the higher deactivation rate when severely hydrocracking jet fuel) and potential consequences in demand and competition for supply.

We find that more stringent controls on aromatics could also adversely impact fuel cost and /or availability. [Chapter 2]

It is important to note that jet fuel is a globally produced and traded commodity and indeed a major proportion of UK jet fuel is imported. Therefore, imposing more stringent requirements over and above international specifications could severely limit availability, increase cost and cause logistics issues such as ascertaining the aromatics content of individual batches of fuel prior to import. Also, a move away from a drop-in solution for fuels would require engine and airframe recertification for use with a very low aromatic fuel and further such fuels may not be compatible with transport and storage infrastructure.

We find that in many emissions studies, the hydrogen content of fuel (percentage hydrogen -%H) is reported as a key variable determining the production of soot. [Chapter 3]

It is important to understand that the hydrogen content of fuel should, in theory, relate to smoke production since it provides the ratio of hydrogen to carbon. However, it is always found to be only a crude proxy for those particular aromatic compounds that result in soot formation and such a bulk carbon: a %H measure can mask the effect of specific molecular structures in the fuel, as molecules with identical hydrogen content can have vastly different soot formation properties. Therefore, while higher hydrogen content indicates a lower relative carbon content and therefore a general trend towards lower smoke production, there is significant data scatter.

We therefore conclude that using hydrogen content as a proxy or regulatory measure for specific fuel molecule types (such as total aromatics and di-aromatics) would carry significant risks. [Chapter 3]

Regulating hydrogen content risks ineffective soot reductions in practice and potential 'gaming' of fuel composition (meeting the regulatory requirement but not the environmental outcome targeted). Too much variability is possible in the composition of fuel to meet a desired percentage hydrogen value. A specification measure requiring a hydrogen content (in terms of %H) for fuel carries risks, since it would be a poor measure of the particular compounds that are believed to be mostly involved in soot formation. However, a calculated hydrogen deficiency (HD) goes some way to addressing this for multi-component mixtures, it is still possible to achieve a target number by a range of chemistries, reducing the benefit of such a HD metric as it cannot replace a more detailed understanding of the fuel chemistry.

The use of the existing methods for specifying the levels of aromatics, di-aromatics and their resultant changes in performance will be more easily adopted by the industry.

Overall, we therefore conclude that further and more stringent constraints than existing specifications on the aromatic content of jet fuel carry significant risks at present.

The factors behind this conclusion are as follows. The environmental outcome is highly uncertain. Limiting aromatic content will significantly increase the cost of refining and producing aviation fuel as well as CO_2 emissions during production of the fuel. The final product will become more like SAF and will reduce the ability of conventional fuels to be blended with SAF. Such constraints would move the fuel to a product presently outside of the experience of the industry.

Recommendations, including future work

1. Improve the evidence base to better understand whether adopting regulatory actions to target soot's role in contrail and contrail cirrus formation would be an effective measure to mitigate aviation's non-CO_2 effects on climate.

This requires large scale international research efforts, as reflected by e.g. announcements of the UK Government's multi-year Non-CO_2 Research Programme delivered by NERC, and ATI, and EU-H2020 initiatives to research the non-CO_2 effects of aviation, and in particular, contrails. In-flight measurements still have a considerable level of uncertainty and do not show a clear relationship between aromatic levels and soot emissions. This requires further investigation. Reductions in aviation soot emissions may reduce the soot aerosol-cloud interaction effect. Currently, this is considered to be a negative Effective Radiative Forcing (ERF) from some model calculations (as large as negative 100s of mW m^{-2}), although some studies consider the effect to be potentially negligible. No best estimate of ERF, in an assessment sense, is possible at the moment. If the effect is shown to exist, then reduction of aircraft soot would logically reduce this potentially negative forcing. By how much is completely unknown, since no baseline is available, nor have soot reduction scenarios been explored.

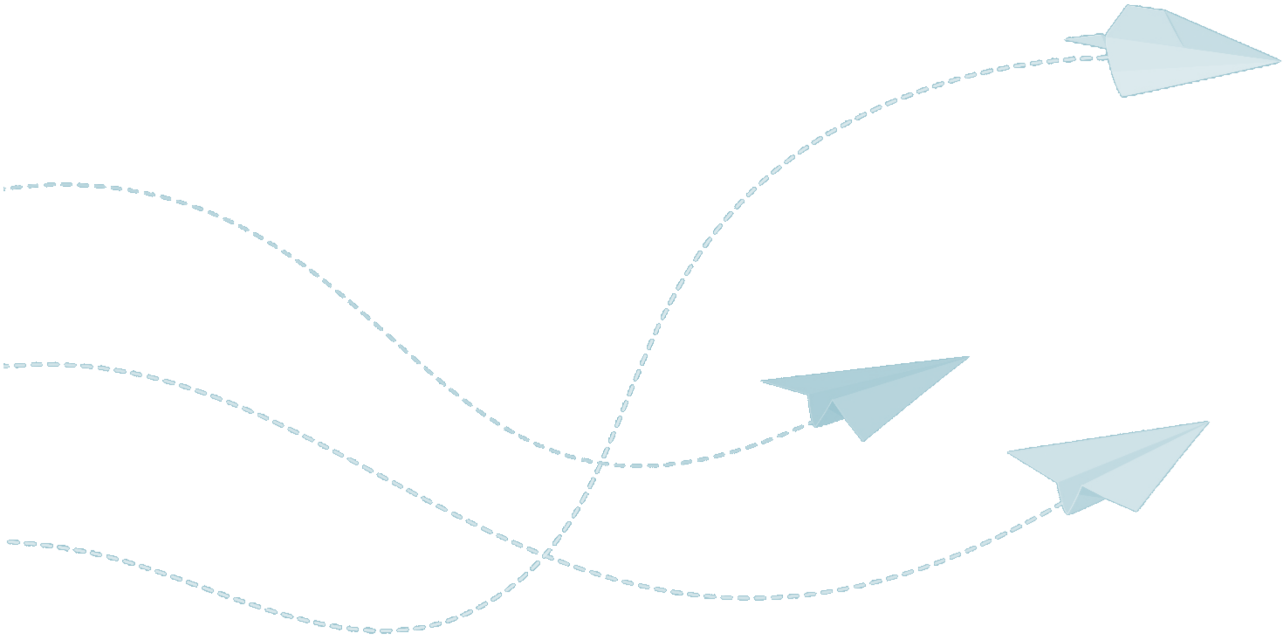
2. Undertake a detailed study (within the existing known uncertainties) of the potential trade- offs between decreased contrails and contrail cirrus by reducing soot emissions compared to increased CO_2 emissions at the refinery.

This will require modelling of additional energy costs at the refinery and exploration of different CO_2-e metrics. This is important since without such a detailed study, there is a significant risk that the environmental outcome is worse than the counterfactual of no regulation. Such a study could be initiated within the UK's academic scientific capability and requires inputs from atmospheric science, fuels and emission technology.

3. Undertake a detailed study of the trade-offs in fuel properties as the aromatic content changes and its viability to be used in aviation.

Studies where one fuel has been hydrotreated to different levels to observe the changes in fuel properties are limited (there are only 3) and only at a pilot plant scale. This is important to assess the extent to which other critical fuel properties are changed by reducing the aromatic content.

Such a study would need to test a small number of representative fuels to then extrapolate the impact on a whole sector, which could be challenging, although it does allow any study to be targeted specifically to investigate properties such as lubricity and thermal stability along with elastomer and soot creation performance

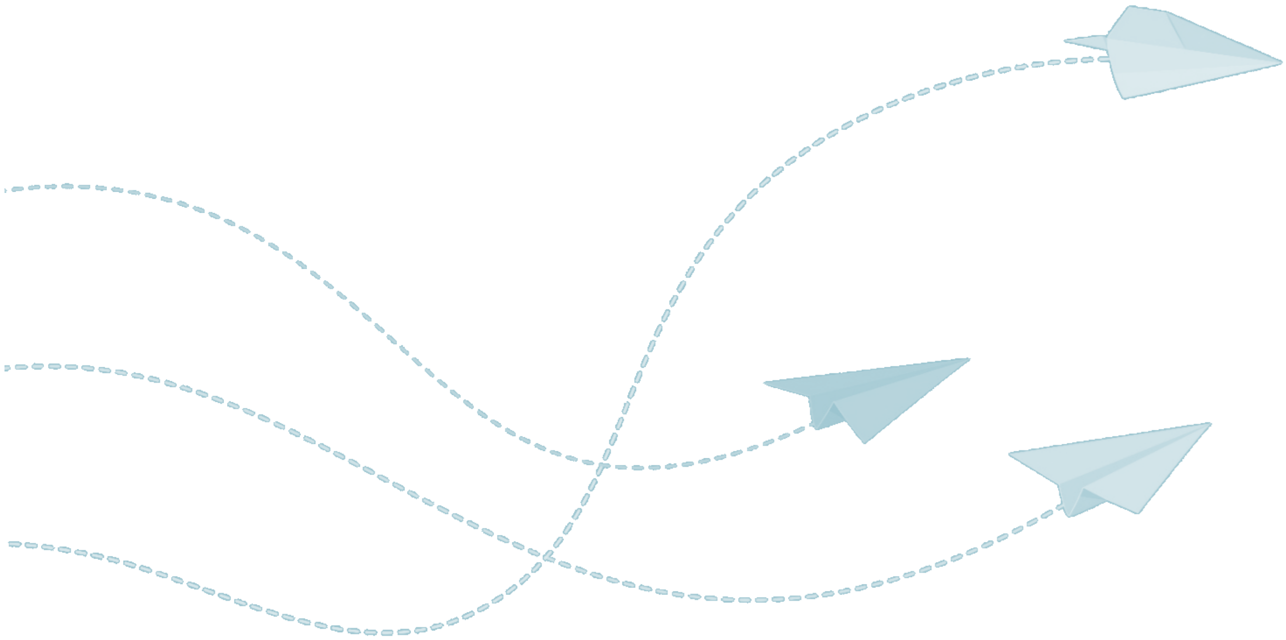


Glossary of terms

Terminology	Definition	Additional Comments / Terminology
AFR	Air Fuel Ratio	An important metric to describe the mass of air in a combustion process relative to the mass of fuel.
API	A commonly used index of density in crude oil refining.	API stands for American Petroleum institute - API is calculated from the specific gravity of an oil using the formula: API = (141.5/specific gravity)- 131.5
ASTM	American Standard Test Methods International	ASTM organisation supports major jet fuel specifications and associated processes and test methods run by consensus of stakeholders. Key specifications include but not limited to: D1655 (Jet A/A-1), D7566 (Control of synthetic and SAF blends), D4054 Process to control evaluation and qualification of new blends.
AtJ	Alcohol to Jet	An approved process for the creation of a synthetic jet fuel blending component from fermented sugars to ASTM D7566.
Blue hydrogen	Hydrogen production from fossil sources such as methane or coal with carbon capture	
CHJ	Catalytic Hydrothermolysis Jet fuel	An approved process for the creation of a synthetic jet fuel blending component from a catalytic route to ASTM D7566.
Contrail cirrus	Cirrus-like cloud that has formed from persistent, linear contrails that have spread into a large cirrus-like cloud.	
CRC	Coordinating Research Council	The CRC is an industry R&D forum that organises programmes to address industry issues and support to ASTM.
Decalin	A di-cyclo paraffin (di- cycloalkane) as shown in Table 2.1	
DEF STAN	Defence Standard (UK specification)	UK MoD Defence Standards define a range of aviation's fuels for commercial e.g. Def Stan 91-091 and military versions. Although independent of ASTM, Def Stam and its committees work in cooperation with ASTM and other international specifications.
Drop in	A fuel from non-fossil sources compatible with the current ASTM D1655 specification and D7566 blending requirements	
EASA	European Union Aviation Safety Agency	Responsible for many aspects of aviation safety (including a role in fuel specification developments, aircraft and engine manufacturers etc) but also the environmental impact of aviation.
EI	Emissions Index	The mass or number of a particular emission per unit mass of fuel burned in the combustion process. A useful way of normalising any emissions data.
FSC	Fuel Sulphur Content usually to ASTM D4294	
FSJF	Fully Synthetic Jet Fuel	Produced from a feedstock not containing carbon from fossil crude or biomass feedstocks.
FT	Fischer Tropsch	An approved process for the creation of synthetic jet fuel blending component to ASTM D7566 .
GC	Gas Chromatography	An electrical technique for analysing the composition of a gasified liquid.
Green hydrogen	Hydrogen production by electrolysing water using renewable electricity (no carbon in the production of fuel)	
GTL	Gas To Liquid fuel production route usually involving FT	
HC	Hydrocracking	Refining process in which higher boiling point components of the refining process are partially or completely converted into lighter, lower boiling point compounds (containing more hydrogen) under the influence of H2 and in the presence of a catalyst.

Terminology	Definition	Additional Comments / Terminology
HEFA	Hydrotreated Esters of Fatty Acid	An approved process for the creation of synthetic jet fuel blending component to ASTM D7566
HiReTS	High Reynolds number Thermal Stability test (ASTM D6811, now expired)	Method of measuring fuel thermal stability, that is the fuel's ability to operate at elevated temperatures without degrading and causing fuel system fouling. HiReTS is used for R&D work only to provide additional insights and not for specification testing (see JFTOT).
HRJ	Hydrotreated Renewable Jet	
HT	Hydrotreatment	A refining process in which impurities in the fuel such as sulphur, nitrogen and oxygen are removed under the influence of H2 and in the presence of a catalyst. Can also result in the conversion of some hydrocarbon molecules into lighter molecules.
hygroscopicity	A material's ability to absorb moisture from the environment	
IPCC	Intergovernmental Panel on Climate Change	
IPK	Isomerised Paraffinic Kerosene	A generic term for synthesised paraffinic kerosene (SPK) that has been isomerised to achieve a lower freeze point.
JFTOT	Jet Fuel Thermal Oxidative Test	Method of measuring fuel thermal stability, that is the fuel's ability to operate at elevated temperatures without degrading and causing fuel system fouling. JFTOT is the current industry standard for measuring thermal stability for specification compliance testing. Fuel must have a JFTOT pass of 260degC to be compliant with Jet Fuel specifications.
JP-8	A military aviation fuel designation, DEF STAN 91-87 similar to Jet A-1 but with additives for military use	
LCA	Life Cycle Analysis	
LCAF	Low Carbon Aviation Fuel	
LCV	Lower Calorific Value or energy density per unit mas (MJ/kg)	This is a measure of the energy content of the fuel expressed as energy per unit mass. The related energy per unit volume can be calculated using the density. Other terms that are used for this property include specific energy, calorific value, heat content etc.
LPP	Lean Premixed Prevapourised combustor technology	
MIR	Mid Infra Red	
MS	Mass Spectrometry	
non drop in	A fuel from non-fossil sources not compatible with the current ASTM D1655 specification and D7566 blending requirements (such as an aromatic content below 8%)	
nvPM	Non volatile Particulate Matter	Strictly, ‘nvPM’ is a defined regulatory measurement under test conditions specified by ICAO.
OEM	Original Equipment Manufacturers	
OH chemiluminescence	The emission of photons (electromagnetic radiation as light) when chemically excited OH molecules decay to ground state following a chemical reaction	
PAH	Polycyclic Aromatic Hydrocarbons	
pilot / mains split	A ratio of mass flow of fuel between the pilot and main flow of a staged combustor	
PM	Particulate Matter	
RF	Radiative Forcing	
RPK	Revenue Passenger Kilometre	
RQL	Rich Quench Lean combustor technology	

Terminology	Definition	Additional Comments / Terminology
SAK	Synthetic paraffinic kerosene containing aromatics	
SARS	Sub-atmospheric Relight Sector	
SMD	Sauter Mean Diameter - a measure of the size of droplets in a spray of fuel	
Specific gravity	A measurement of density, calculated as the ratio of the density of a liquid to the density of water	
SPK	Synthetic paraffinic kerosene	
spray cone angle	The angle across the entire spray of droplets created by a fuel atomiser in an engine	
straight run fuels	A refining term to indicate a fuel produced with no hydrotreatment following distillation	
TAPS	Twin Annular Premixing Swirler combustor technology	
TRL	Technology Readiness Level	
vPM	Volatile Particulate Matter	



1. Introduction and background

Summary

In this chapter, the outline and background issues associated with mitigating the effects of aviation non-CO_2 emissions on climate are presented. Aviation affects climate through CO_2 and also through non-CO_2 emissions, which include nitrogen oxides (NO_x), water vapour and aerosol particles (which may be classified as ‘volatile’ and ‘non-volatile’; the former from sulphur and condensable organic compounds, the latter from soot). At present it is thought that the largest quantifiable non-CO_2 effect of aviation is from ‘contrails’, which are formed by the condensation of emitted water vapour on soot particles in the exhaust, rapidly freezing at cruise-type altitudes and taking up water vapour from the background atmosphere to initially form line- shaped ice crystal clouds, occasionally spreading to form a cirrus like cloud coverage. It is thought that contrails and ‘contrail cirrus’ warm the atmosphere, overall, but the phenomenon has large scientific uncertainties. One means to reduce contrails might be to reduce the soot particles in terms of their number emissions (how many particles), and there is evidence that they can be reduced by reducing the ‘aromatic’ content of the jet fuel. This would decrease soot particle number, and by inference, reduce the abundance of ice crystals formed, and the consequential effect of contrails. The report explores these considerations and details the evidence and mitigation potential, with this chapter providing the scientific, technological and policy background.

1.1. Challenge statement

The background ‘challenge statement’ to this report is to undertake a literature review and assess whether reducing the aromatic content of jet fuel (kerosene) would reduce contrails and have a net climate benefit. The assessment seeks to identify the costs, safety, and operational implications of reducing the aromatic content of jet fuel to different levels and clarify the trade- offs between any extra CO_2 emissions generated during the hydrotreating process and the potential for reducing climate warming contrails.

1.2. Report structure (in brief)

Chapter 1: Provides the background to the environmental issues, the existing fuel specifications, stakeholders involved and points forwards to where these issues are addressed.

Chapter 2: Introduces concepts on fuel composition and measurement methods.

Chapter 3: Discusses fuel production methods, present composition and required properties of the fuel.

Chapter 4: Outlines the impact of aromatic compounds on engine and airframe systems and the consequences of reducing the aromatic content of fuel through hydrotreatment / hydrocracking. In addition, the replacement of aromatics with cycloparaffins is discussed.

Chapter 5: Discusses how fuel is delivered to the engine, is combusted, and how the emissions are formed.

Chapter 6: An overview of the climate impact of the resultant emissions discussed in previous chapters, and how they relate to fuel composition.

Chapter 7: A summary of findings, and recommendations.

1.3. Background

Aviation has several effects on climate through its CO_2 and non-CO_2 emissions. Emissions of CO_2 and its effects are well quantified and understood, and there are already a number of initiatives in place through UK national and international policy to address CO_2 emissions through technological programmes such as the International Civil Aviation Organization's CO_2 emissions standard and market-based measures such as the UK and EU emissions trading schemes for aviation and ICAO's Carbon Offsetting and Reduction Scheme for International Aviation [CORSIA]. There are also a number of major initiatives to introduce 'Sustainable Aviation Fuels' (SAF), where the aim is to produce a fuel that has lower life cycle emissions savings compared to petroleum- based kerosene (Jet A/A-1). Furthermore, there is growing evidence that SAF also has benefits in use, in terms of non-CO_2 benefits and potentially some CO_2 savings. Such initiatives and targets for SAF have been proposed by government and industry and there is work happening both domestically in the UK and internationally to address aviation's CO_2 emissions. Further, the government is implementing a SAF mandate from 1 January 2025 which sets the overall SAF demand at 2% of aviation fuel supplied in 2025, increasing to 10% in 2030 and 22% in 2040.

Non-CO_2 emissions from aviation affecting climate include water vapour, nitrogen oxide emissions (NO_x, where $NO_x = NO + NO_2$), soot and sulphate aerosols, and result in a range of effects that alter atmospheric composition, aerosol loading of the atmosphere and perturb cloudiness. One of the potentially largest current non-CO_2 effects (with large uncertainties) is the formation of condensation trails (contrails) behind aircraft at cruising altitudes, formed from the initial condensation of emitted water vapour on particles also emitted by aircraft engines, especially soot. These droplets rapidly freeze under the cold conditions typically found at cruise altitudes and under certain atmospheric conditions of high humidity (ice supersaturation), can grow to form ice crystals which may persist, resulting in large ice crystal clouds that spread into cirrus-like clouds (contrail cirrus). Large 'outbreaks' of contrail cirrus can occur in certain weather situations in highly trafficked regions and are clearly visible.

Because aviation's non-CO_2 effects on climate at altitude have been difficult to quantify with a reasonable degree of confidence, it has thus far been difficult if not impossible to put in regulations based on sound science. Nonetheless, there is growing evidence that in the case of contrails and resultant contrail cirrus, the effect is related (in some poorly quantified manner) to the number of soot particles emitted by the current fleet, which in turn is related to the chemical composition of jet fuel as well as the combustion conditions of the engine (which is better quantified). Much of this evidence has been gathered from measurements of soot number concentrations in jet exhaust, mostly at ground level but also from limited observations at altitude. Most of this recent evidence has been gathered during SAF evaluations which are known to have a different chemical composition to conventional fossil Jet A/A1 but have some similarities to low aromatic conventional fuels. The evidence suggests a relationship between soot particle numbers, the 'aromatic' content of the fuel and the aircraft engine combustor design. This observation has led to suggestions that a reduction on the aromatic content of fossil- based fuel through an industrial process called 'hydrotreatment' (which requires a source of hydrogen) may reduce soot emissions, and contrails. The basis of this evidence is assessed in this report to provide a better understanding of this relationship.

'Soot' is what is referred to as the observed emission that has a range of effects; 'Non-volatile particulate matter' (nvPM) is a regulatory parameter that has highly specified measurement conditions (by ICAO) under ICAO Annexe 16. In the atmosphere, this equates to 'soot', which is defined here as a mix of black and organic carbon. Soot is emitted in aircraft engine exhaust as very small particles, mostly under 100 nm in diameter. In the literature, 'black carbon' (or BC) is sometimes used interchangeably with soot. Here, 'soot' is preferred since it encompasses organic compounds as well.

Ultimately, the source of soot is the fuel chemical composition, although the role of the combustor design should not be neglected. Conventional aviation fuel (Jet A/A-1) is a complex mixture of hydrocarbons and is produced predominantly from sources including crude oil and other fossil sourced feedstocks. Crudes historically used by refineries in the UK and EU from the North Sea ("Normal Crude" e.g. Brent Crude) have an aromatic content between 20-40%. As North Sea crude oil production is dwindling alternative crudes with higher aromatic and asphaltene content are being used adding a further complexity to the aromatic composition and a greater need for hydrotreatment. In the UK there are currently six refineries of which Fawley is the largest, processing 270,000 barrels of crude each day and has a direct jet fuel pipeline to Heathrow. Hydrocarbons are chemical compounds containing hydrogen and carbon. These molecules fall into the broad compositional classes of n-paraffins, iso-paraffins, cyclo-paraffins (which have a saturated ring) and aromatics (unsaturated ring), which have either a single aromatic ring or multiple aromatic rings. These multi-ring classes are often referred to generically as di-aromatic (or naphthalenes), but this term normally encompasses 2 or more aromatic rings; a detailed description of these classes will be provided in Chapter 2.

In addition to these bulk species, fuel refined from crude oils often contains trace levels of other species, particularly sulphur and nitrogen containing polar and heteroatomic species which although present in low concentrations both positively and negatively affect the performance of the fuel in the airframe and engine and need also to be investigated. These materials are removed by hydrotreatment.

Of interest in these studies are the aromatics which unlike the paraffins have a higher proportion of carbon and they are unsaturated and consequently are more difficult to burn completely without production of soot and particulates. They represent a key challenge to combustion systems in that the conditions must be hot enough and have sufficient residence time to ensure complete combustion, but such conditions promote the formation of NO_x. Combustor designs therefore must have a balance/compromise that is discussed in detail later.

This complex mix is produced from the refining of petroleum crude oil. The specific combination of hydrocarbon species in the fuel depends on many factors including the crude characteristics, refinery capability, and the products of the refinery. Whilst the aviation fuel product is optimised to meet primary specification requirements the refinery output composition to achieve this can vary significantly from refinery to refinery. It is important to put in context that typically only 4- 6% of a barrel of crude ends up as aviation fuel and that refinery production balance is often mainly driven by other factors such as overall yield, efficiency, commercial issues, and, often products that represent the major output such as diesel and petrol. Note that aviation fuel sits between these two products and like all such products is an agreed compromise between producers and users.

The choice of refinery technology employed is dictated by the above balance but normally includes at various stages, fractionation to separate the required boiling range or "cut" and means of product improvement/upgrading which may include hydrotreatment or more severe hydrocracking which are of most relevance for this study as well as caustic wash treatments. Note that the capacity and use of hydrotreaters and severity of processing will be based on the technical demand for each of the key products and note that capacity is mostly deployed by the need for very low sulphur levels in automotive diesel fuels as hydrotreating is an energy and hydrogen intensive process.

Hydrotreating has other benefits in terms of fuel performance but can also have some negative impacts. It should be noted that modern refineries, despite being highly complex systems that are operated to tight controls on conditions, are very efficient at what they do. They are driven to this high efficiency to be economically viable and provide the slate of products required from the crude supplied. Any change to these factors such as reducing aromatics in jet fuel as reviewed in this report has the potential to require re-configuring refinery hardware, changing refinery operating conditions which could affect the overall efficiency and therefore the environmental impact and commercial viability, but most importantly will alter other fuel properties of both jet fuel and other products made alongside.

The current challenge, and the remit of this report, is to examine if by changing the specification controls on aviation fuel combustion related properties there would be potential to reduce smoke, particulate and contrails. These controls could be based on total aromatic, naphthalenes, a combination of these or other combustion related parameters such as smoke point. However, it is recognised that this could mean more intensive refining, primarily hydrotreating, which would entail increased environmental impact in production and possibly affect refinery costs and yield. Further, such intensive processing will impact on other fuel properties that could be both positive and negative. This report aims to examine all of these issues to understand the feasibility, risks and benefits of more stringent controls on combustion related properties from refinery production through use in current aircraft and finally impact on emissions.

More specifically, this work should investigate and evaluate the following:

1. Evidence to understand the relationship between lower aromatic content and non-volatile Particulate Matter and, therefore, contrail impact.
2. Costs of adapting the hydrotreating process and operational impacts of lower aromatic content in kerosene, including longer-term cost trade-offs on maintenance/ longevity of engines.
3. Finding the optimal mix of aromatic content (%) to balance soot-forming potential, production costs and other performance properties of the fuel.
4. Assessing current sulphur levels in jet fuel, and the impact of different levels on the climate, with the objective of maximising benefits.
5. Recommendations on how to ensure engines are compatible with lower aromatic content without any negative impact on engine performance including elastomeric seal leaks.
6. Investigating the lifecycle emissions of reducing the aromatic content of jet fuel and establishing if there is a CO_2 trade-off due to extra energy expended at the refinery, and whether that risk outweighs the benefit of reducing non-CO_2 impacts.

The scope of this report has been confined to conventionally derived aviation fuel produced from the allowable conventional (fossil) crude oil sources. Although some of the data used refers to neat synthetic paraffinic kerosenes (SPK)s and sustainable aviation fuel (SAF) blends, these are used as an analogy to lowering aromatics levels, see below, but are not part of the overall analysis of the impact of lowering aromatics levels of conventional fuels.

Furthermore, whilst there are currently discussions regarding Low Carbon Aviation Fuels (LCAF) detailed analysis of this subject is outside the scope of this report. LCAF a definition of ICAO and is concerned with running the refinery in a more environmental way (such that the Greenhouse Gas (GHG) impact of fuel production is at least 10% lower than current conventional fuel refining) but the final product of jet fuel would, all things being equal, remain essentially the same. It should be noted that the incremental change in terms of hydrogen consumption and energy requirements discussed in this report to reduce aromatics etc would be essentially the same for LCAF run refineries as conventional refineries. However, the predicted increase in process intensity may well counter the benefits of having a LCAF based refinery.

To meet the above requirements the report develops an understanding of what aromatics are, how and why they are in the fuel, their impact, and the impact of their removal, on both the target property of combustion but also their effect on other fuel properties and performance that affect refinery, distribution and use. These effects are both directly due to the reduction in aromatics but also the "side effects" of hydrotreating on other components and trace materials. Finally with an understanding of their impact on combustion systems and subsequent emission the report develops an understanding of the link between fuel aromatics and smoke and particulate production, and their potential impact on global environment. Also affected by many of the same emissions is the local air quality, however this is outside of the scope of this report. From this, a strategy for considering future aromatics content monitoring and control through fuel specifications can be based on clear understanding of the science and further the overall risks and benefits can be assessed.

The majority of this study is based on summarising and collating data, information and knowledge from a range of sources and these sources are clearly referenced. It is important to note that many of the tests in the fuel specification are not absolute measurements of a fuel's property or composition. They do however represent the best available, reliable test method available at the current time. As a key part of this study fuel composition is discussed through the report but Chapter 2 will focus on how aromatics are measured and controlled now and the prospective for changes in the future.

There is very limited parametric type data on the change of fuels from the same source but having been subjected to varying degrees of hydrotreating. Only three studies have been identified and will be discussed in Chapter 3 along with potential for some additional laboratory testing to address this gap in the literature. However, there is a large bank of information on the impact of blending conventional fuels with varying levels of SPKs, generally up to 50%, which are in effect zero aromatics. This therefore reduces aromatic content by dilution and changes other fuel properties in a similar way due to the increase in paraffinic hydrocarbons. Thus, this gives a good indication of the likely changes but must be taken in context that it is not exactly the same and perhaps may lead to the conclusion that more work needs to be done in this area.

1.4. Fuel specification

Current specification requirements for fuel which can be used in aviation define the fuel in terms of bulk composition, trace materials and some direct performance properties. Jet fuel is a commodity so stringent definitions of a chemical composition for aviation fuel that had to be tested on every batch would limit the supply of fuel and increase the cost of fuel production. Instead, the specification requirements for aviation fuels focus on a number of relatively rapid tests which can be performed to assess a combination of physical properties of the fuel (such as density and viscosity) and a small number of chemistry test (such as aromatic content, sulphur content and acidity) and some key performance requirements such as lubricity, thermal stability and freeze/flash point. A full list can be found in typical internationally recognised specifications such as Defence Standard 91-091 or ASTM D1655.

As the efficiency of the turbomachines used in aviation has improved, the desirable qualities of fuel for aviation have become refined and established into the fuel specification, providing a link between fuel chemistry and fuel performance. However, it is important to note that the fuel specification is analogous to a quality control check of fuel leaving the refinery and arriving at the aircraft, it is not a complete list of all fuel properties of importance for the entire fuel system. It suffices for situations where fuels are from energy sources similar to the aviation fuel in use today. The specification also identifies when the production of the fuels strays too far from the expected fuel property and performance norms for which aircraft and engines are designed and ultimately certified.

Whilst the basic requirements of the fuel are rigorously defined and controlled, the combination and variation of chemical species which can result in fuels meeting these limits is large given all the above variables and factors controlling production. As a result, despite varying actual composition the predictable behaviour will be within accepted norms and therefore be suitable for use in the fuel supply chain network, storage tanks at airfields, on wing and in the engine (these behavioural properties are referred to as “fit for purpose properties”)

1.5. Stakeholders and wider perspectives

From an aviation fuel industry perspective, fuel specifications are considered as the minimum standard of jet fuel that has been agreed by all stakeholders from refineries, through distribution and ultimately in the aircraft and engines. Whilst the specification sets a high minimum standard it must allow both flexibility and, in some respects, have compromises to ensure the product is available in sufficient quantity, can be produced globally and can be manufactured and transported to the final user in a fit for purpose state at an acceptable economic cost. Figure 1.1 shows the key stakeholders and influencing factors that have driven specifications to where they are today.

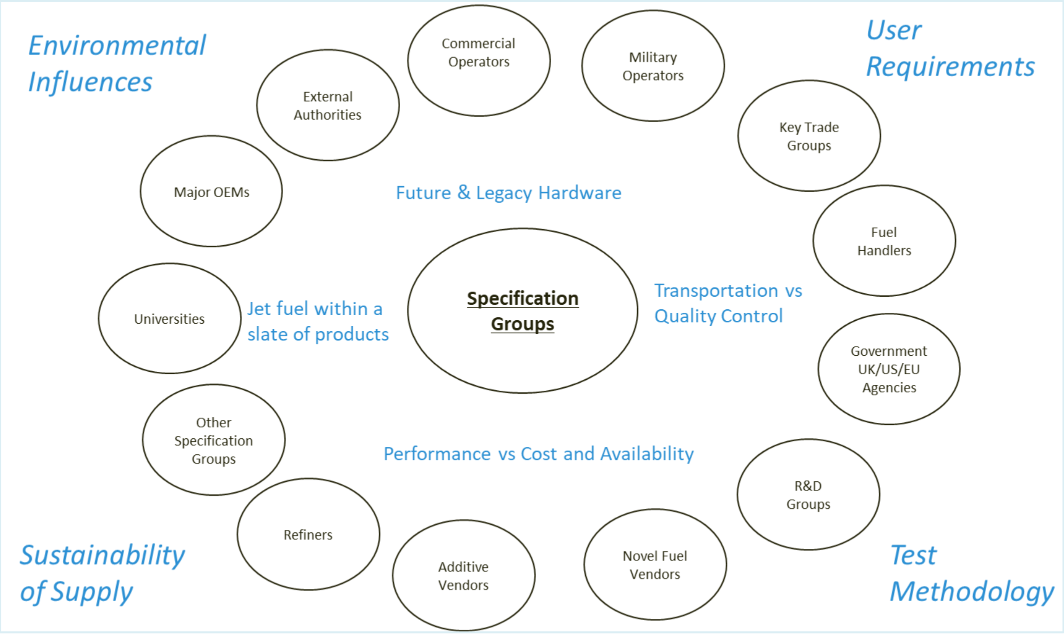
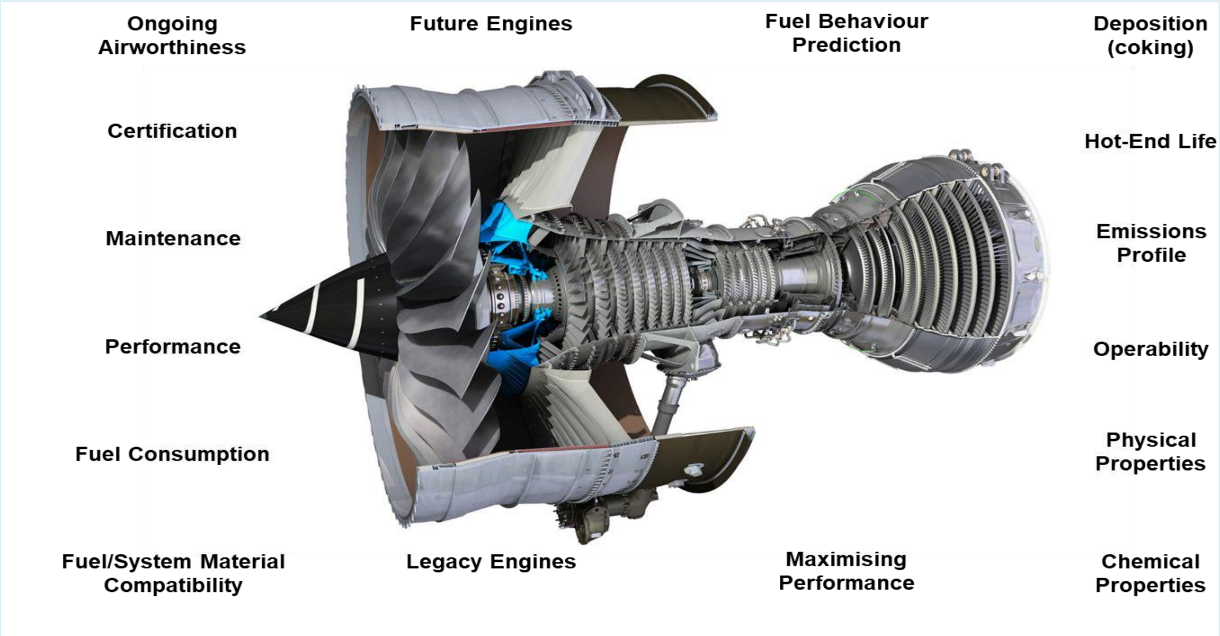


Figure 1.1: Industry stakeholders and influencing factors

Significant changes to the specification can upset the balance of these factors, and such change needs to be considered carefully as changes in one target property, such as reducing aromatics, will have impact on other fuel performance properties and cost of manufacture, yield etc. It is also important to keep in mind that aviation fuel is a global commodity so the impact of changes in specification requirements in one geographic region can have unforeseen consequences for the global supply chain and/or airline operations.

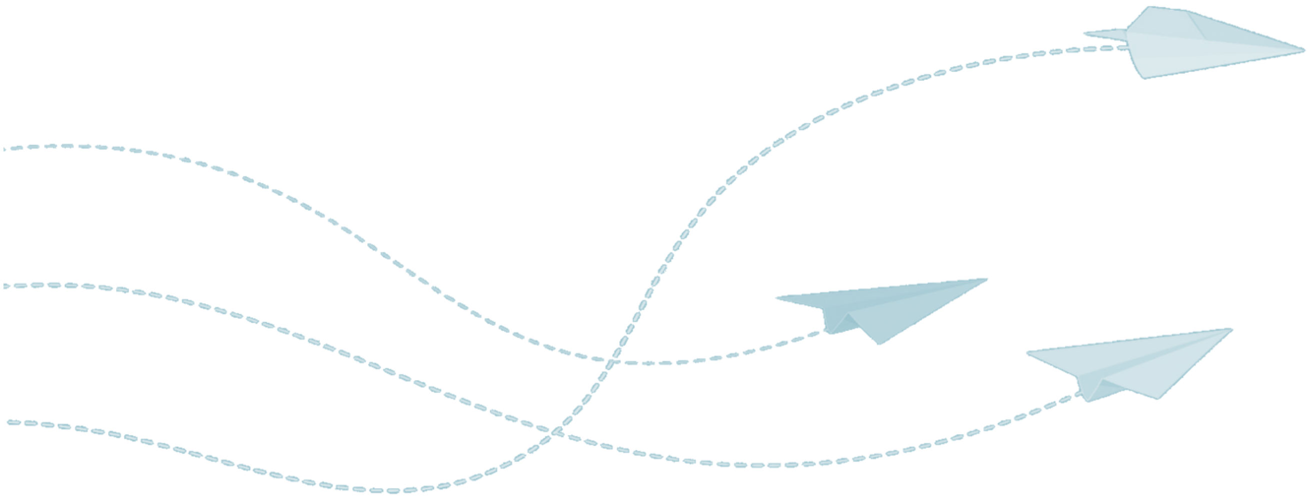
From an aircraft and engine perspective, fuel performs many functions within the airframe and engine apart from the obvious role of providing thermal energy from combustion. In both the airframe and engine fuel can be subject to very challenging conditions before eventually being burnt in the combustion system and in addition, must be fully compatible with all system and component materials. Fuel properties and performance can have a significant impact on fuel delivery, combustor and turbine operability, performance, and service life and therefore cost of ownership and airworthiness. An example of these impacts on a gas turbine is shown in Figure 1.2, to provide examples of all the performance properties of an engine affected by the fuel and its composition.



XWB cutaway courtesy of Rolls-Royce plc

Figure 1.2: Impact of fuel properties and performance on a gas turbine

Following combustion of the fuel, the emissions from the engine will interact with the environment resulting in change in local air quality (during the taxiing, take-off and landing cycle) and changes in the composition of the atmosphere (during climb out, cruise and descent).



2. Introduction to fuel composition and measurement methods

Summary

Jet fuel, or kerosene, is a complex liquid fuel, largely produced from fractional distillation of crude oil, a fossil source. Its composition and performance is determined by international standards, set to satisfy the demanding requirements for aircraft and engine combustion efficiency, operability and safety. This chapter describes jet fuel composition in detail, including the chemical nomenclature of the compounds present, and their specific properties. This is necessary to understand how the fuel is produced and link to the different components and performance, since they are not independent. ‘Aromatic’ compounds are naturally present in fossil crude oil and the jet fuel derived from it and thought to be largely responsible for soot emissions. The concept of ‘hydrogen deficiency’ is introduced, which quantifies the lack of saturation of aromatic compounds with hydrogen, which hydrotreatment increases, altering the nature of the aromatic compounds. While aromatics do not have as great an energy density (per unit mass) as other components in jet fuel, they are essential for current aircraft fuel systems in terms of a range of properties and ensuring integrity, since they provide elastomeric seal swell. The types and properties of the variety of aromatic compounds found in jet fuel are described and quantified along with the measurement methods and test standards available, since any change in the aromatic content needs to be understood in the context of how these compounds are measured, and the availability of facilities for doing so. It is shown that current specification test methods only provide information on aromatics in terms of total content, single and multi-ring types rather than detailed information on specific aromatic compounds. It is likely that if a specific aromatic compound, or compounds, were to be targeted for measurement in the context of a requirement for reduction, significant costs would be incurred for new test facilities that would be required across the fuel supply chain.

2.1. Introduction

Any change in fuel processing to reduce the level of aromatics will have an impact on the chemical composition of fuel. This chapter sets out a description of the composition of typical fuels from a fundamental perspective as this is helpful when interpreting the subsequent chapters which focus more on the means to produce fuels of varying compositions and their subsequent properties and performance.

In addition, this chapter sets out an overview of the measurement techniques used to establish the aromatic content of fuel in addition to other key compositional measurements for fuels which will be relied on in later chapters.

2.2. Fuel composition

Conventional jet fuels are composed of two categories of chemical classes, bulk chemical constituents and trace components. Trace components are typically at very low levels and controlled directly by specification test requirements and limits e.g. sulphur up to 0.3% mass or by key performance measures such as thermal stability and lubricity (described in Chapter 4). The major bulk hydrocarbon constituents are grouped in six broad classes shown in Table 2.1, including linear alkanes (n-alkanes), branched alkanes (iso- alkanes), cyclo-alkanes, and aromatic compounds. The aromatic compounds encompass alkyl aromatics, cyclo-aromatics, and di- aromatics (or Naphthalenes). A typical distribution of these classes (or structures) of hydrocarbons, in terms of carbon number (carbon chain length) and the mass % are illustrated in Figure 2.1. A more detailed list of hydrocarbons is provided below.

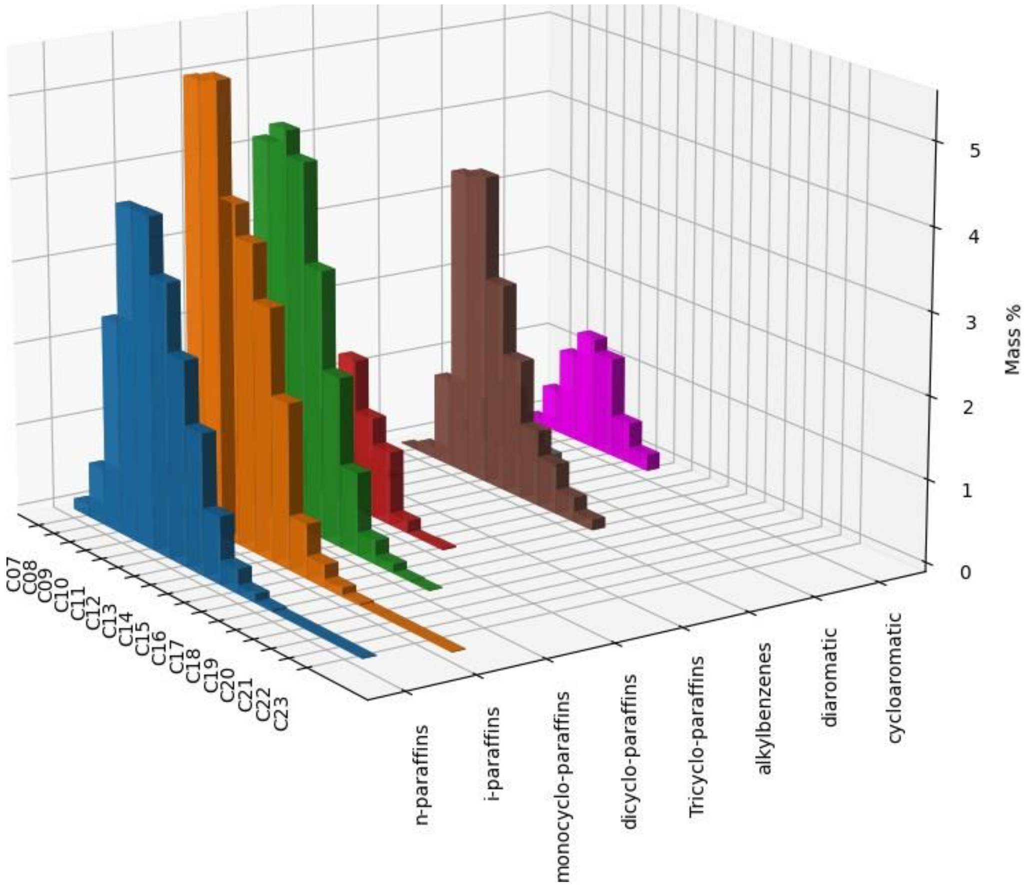


Figure 2.1: Distribution of these classes of hydrocarbons, in terms of carbon number and the mass%

Examples of these four classes of hydrocarbons which form the bulk of the aviation fuel chemistry are shown in Table 2.1, along with a simplified chemical formula which indicates the difference in the structures. The normal alkanes are the simplest molecules with a straight chain of carbon atoms with single connections between adjacent carbon atoms (saturated) and all remaining bonds are attached to a hydrogen atom. The iso-alkanes have the same form, but the carbon atoms are “branched” rather than forming a straight chain. Cycloalkanes are loops of saturated carbon atoms, although they do contain less hydrogen than normal- or iso- paraffins as they are formed into a ring of carbon atoms. Cycloalkanes can connect to normal and iso-alkane chains as well as to other cycloalkane loops. Saturated hydrocarbons do not contain any double/triple bonds between carbon atoms.

Aromatic compounds are unsaturated cyclic compounds with alternating single and double bonds between carbon atoms and are typically a more compact, higher density molecule. Various examples of more complex structures found in fuel are shown in Table 2.1, indicating that these structures can repeat and be joined together. In Jet A/A-1, aromatics do not feature in larger structures than di- or tri aromatic rings although the crude oil source they are refined from can contain significantly larger molecules.

Note the difference between Naphth***e***ne and Naphth***al***ene, alternative names for cyclo alkanes and di aromatics respectively.

These molecular structures determine the physical properties of the fuel and the emissions behaviour when combusted in a practical combustor. The more complex the structure, the harder it is to break down in the combustion process and the more likely that partially combusted elements of the structures will contribute to a soot emission.

Conveniently characterising the complexity of these molecules in a single variable is challenging, particularly for studies looking to relate fuel chemistry to other properties. One convenient reduction used in the literature is the concept of hydrogen deficiency (HD) which is characterised by the formula [1]:

$$HD = (x+1) - \left(\frac{y}{2}\right) \tag{1}$$

Where the x and y come from the generic chemical formula C_xH_y for a hydrocarbon. The HD is therefore a measure of the amount of cyclic and unsaturated molecules present in the fuel. Therefore, increases in HD indicate a propensity for the formation of smoke / soot during the combustion process – such as the structures of di-aromatics (Naphthalenes) which have a HD of
8. This will be expanded upon in Chapter 5. The concept of HD is also useful for an understanding of the refinery hydrotreatment process, which essentially adds more hydrogen to the fuel molecules where there is a deficiency. Hydrocarbons with a higher HD are preferentially removed by the hydrotreatment or hydrocracking processes.

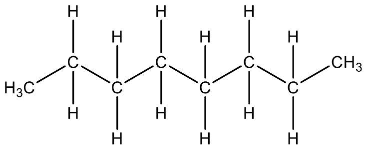
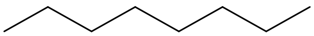
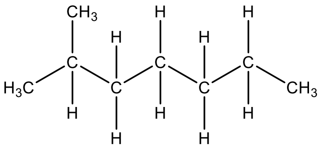
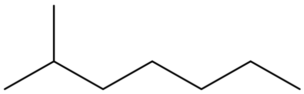
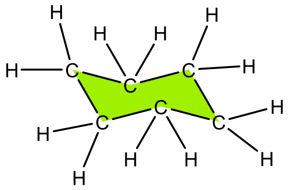
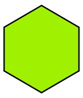
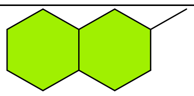
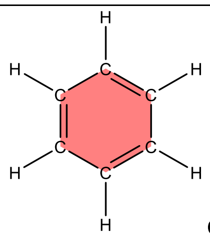
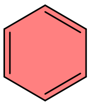
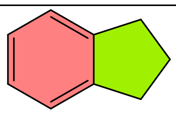
The combined HD for a real fuel can be estimated from a mass weighted summation of the HDs of its components, or more simply, it can be calculated from an assumed molecular formula in the form C_xH_y. The application of this measure to real fuels will be discussed in Chapter 3 and is based on the measurement techniques addressed later in Chapter 2.

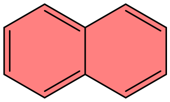
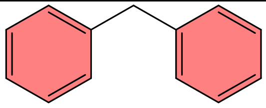
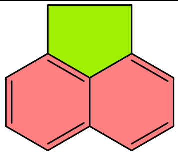
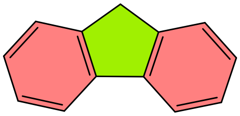
To further characterise the molecular chemistry of fuels, it is also important to define some additional terms:

- alkyl- the prefix alkyl is used to mean an alkane group with one carbon atom missing. The smallest alkyl group is $-CH_3$, which can be seen at the terminal positions of molecules in the n-P group, although they can appear in any of the molecular forms shown in Table 2.1, for example alkylbenzene as shown in Figure 2.2 below.
- Cis- and trans- are prefixes which determine the location of any functional group in the terminal positions of a molecule. Cis- indicates that the functional groups are on the same side of the molecule, trans- indicates that they are on the transverse (opposite) sides of the molecule.
- R is an abbreviation for Radical and represents any group in which a carbon or hydrogen atom is attached to the rest of the molecule, such as a methyl (CH_3) group

Table 2.1 shows the theoretical percentage hydrogen content (by mass) of the typical molecules found in aviation fuel. For pure fuels, made up of only one hydrocarbon structure, the percentage hydrogen content by mass (%H) content would drop linearly as the HD increases. However, for real fuels, made up of a range of structures and carbon numbers (as shown in Figure 2.1), the same %H can be achieved by many different combinations of composition which can result in a range of property values and performance characteristics. For this reason, it is not advisable to consider measured %hydrogen content as a direct substitution for the measurement of specific classes of components in the fuel, such as "aromatic content" which covers the classes containing at least one aromatic ring.

Table 2.1: Typical hydrocarbon compositions including theoretical Hydrogen Deficiencies, %H content and carbon to hydrogen ratio (in brackets) by mass of particular structures.

Symbol	Description	Chemical Structure	HD	%H* (C/H ratio) (mass)
n-P	Normal alkane (linear, normal paraffin) Formula: C_nH_{2n+2}	 Simplified structure: 	0	15.3852 (5.50)
i-P	Iso alkane (branched, iso paraffin) Formula: C_nH_{2n+2}	 Simplified structure: 	0	15.3852 (5.50)
N	Cyclo alkane (Naphthene) Formula: C_nH_{2n}	 Simplified structure: 	1	14.3719 (5.96)
diN	di-cyclo alkane (di-naphthene or decalin) Formula: C_nH_{2n-2}		2	13.3339 (6.50)
mAr	Mono-aromatic (+alkyl substitution) Formula: C_nH_{2n-6}	 or: 	4	11.1806 (7.95)
NmAr	Naphthenic mono-aromatic (+ cyclo alkane ring) Formula: C_nH_{2n-8} (for n ≥ 9)		5	10.0633 (8.94)

Symbol	Description	Chemical Structure	HD	%H* (C/H ratio) (mass)
diAr	di-aromatic (Naphthalene) Formula: C_nH_{2n-12} (for $10 \leq n \leq 12$)		7	7.7423 (11.92)
	Formula: C_nH_{2n-14} (for $n > 12$)		8	6.5362 (14.30)
NdiAr	Naphthenic di-aromatics Formula: $C_{12}H_{10}$ (for $n = 12$)		8	6.5362 (14.30)
	Formula: C_nH_{2n-16} (for $n > 12$)		9	5.2983 (17.88)

Calculated for n=12

The relative proportions of these classes play a significant role in determining the properties and performance of jet fuel. These include but are not limited to combustion, storage and thermal stability, metering and aircraft range, atomisation, fluidity at low temperature, compatibility with elastomers, and general handling and will be addressed in the subsequent chapters.

Table 2.2: Comparison between molecular classes

Component	Benefits	Drawbacks
Normal-alkanes	Low molecular density High energy content High hydrogen content High deposition stability	Poor freeze point behaviour Poor storage stability
Iso-alkanes	Moderate molecular density Good freeze point behaviour High deposition stability	Higher cost of isomerisation (if produced synthetically) Poor storage stability
Cyclo-alkanes	Higher molecular density Moderate storage and deposition stability	Moderate freeze point behaviour Low hydrogen content
Aromatics	High molecular density High seals compatibility	Soot propensity Low hydrogen content
Di-aromatics	Highest molecular density	High soot propensity Low hydrogen content
Trace species	Contributes to good lubricity behaviour Contributes to good storage stability (anti-oxidants)	Contributes to thermal stability deposition

Of particular interest are the di-aromatics (Naphthalenes) in Table 2.2, as these are the lowest hydrogen content materials in the fuel, they are the first to be affected by increased hydrotreatment of the fuel. Note also that trace species will also be reduced by hydrotreating along with the naphthalenes. Importantly, the current level of hydrotreating capacity is not used to target the removal of aromatics. Hydrotreating capacity in Europe is currently installed and used for producing ultra low sulphur, Euro 6 diesel to EN 590, rather than a reduction in aromatic content, although the hydrotreating step may also reduce aromatic content to some degree. Understanding how we measure and control/limit these components of fuel is an important step in understanding how their concentration in compliant fuels can be monitored and potentially regulated.

Any proposed correlation between the chemical composition of jet fuel and its properties needs careful justification, and suggested relationships based on one compositional property alone (such as aromatic content) are necessary oversimplifications of a complex series of relationships. Machine Learning methods permit the investigation of multiple compositional variables simultaneously and have been successfully used to predict a limited but important subset of fuel specification properties [2]. However, an understanding of these relationships is far from intuitive. In a similar manner, the selection of a fuel composition on the basis of one fuel performance property alone is not adequate and a range of fuel performance properties must be balanced in any recommended composition change. For instance, n-alkanes and iso-alkanes impart high energy density per unit mass (Chapter 3) and thermal stability (Chapter 4). However, the ratio of these same components present restrict the low temperature properties and handling behaviour which limits the allowable level of n-alkanes in both conventional fuels and SAF based blends.

Specific iso-alkane/cycloalkane ratios have the potential to increase both energy density by unit mass and by unit volume of jet fuel blends [3]. This is well addressed in development of proposed novel high-performance SAFs (sometimes called Advanced fuels) which are cyclo-paraffinic and can currently only be blended at up to 10% with conventional fuel [3], [4]. These products are different compositionally from straight SPK fuels such as HEFA and FT SAFs as they are predominantly cycloparaffinic in nature rather than n- and iso- paraffinic. These products may provide an alternative component to allow for a reduction in aromatic compounds (by volume) while adding target iso-alkanes and cycloalkanes to meet a drop in fuel specification i.e. that can be used in current aircraft. The replacement of aromatics with cycloalkanes will be discussed in detail in Chapter 4.

2.3. Definition of aromatics

The term “aromatics” in the context of fuel composition and associated test measurements covers any and all molecules that contain at least one unsaturated aromatic ring (see cycloaromatic in Figure 2.2 below). Is important to note that in the jet fuel boiling range, benzene, a single ring only with no alkyls (paraffinic) chains or cyclic rings attached, would not be present as it is too volatile and would be excluded by volatility controls. Therefore, every aromatic molecule in jet fuel will have one or more alkyl chains attached to the point where the boiling point is within the range of jet fuels. These chains may be straight, branched, or cyclic as these combinations are present in crude oil and pass through to the final product during refining but are acceptable for jet fuel. Examples are shown in Figure 2.2 and are all included in the ASTM D1319 method for measuring total aromatics [5] as required for the specification of Jet A/A-1.

Within specification testing there is also a separate method to measure compounds with two or more unsaturated rings, ASTM D1840 [6]. This di-aromatic class of components are measured separately since their impact on smoke and particulate production is much greater than for single ring compounds. In the Jet A/A-1 specifications, “total aromatics” includes single and multi-ring compounds and has a maximum of 25% (by volume) by ASTM D1319 but the multi-ring compounds are limited to 3% (by volume) directly by ASTM D1840 or indirectly by smoke point. This allowance controls soot propensity in the most cost-effective way and the method represents the currently available control and monitoring measurement for aromatic content around the world.

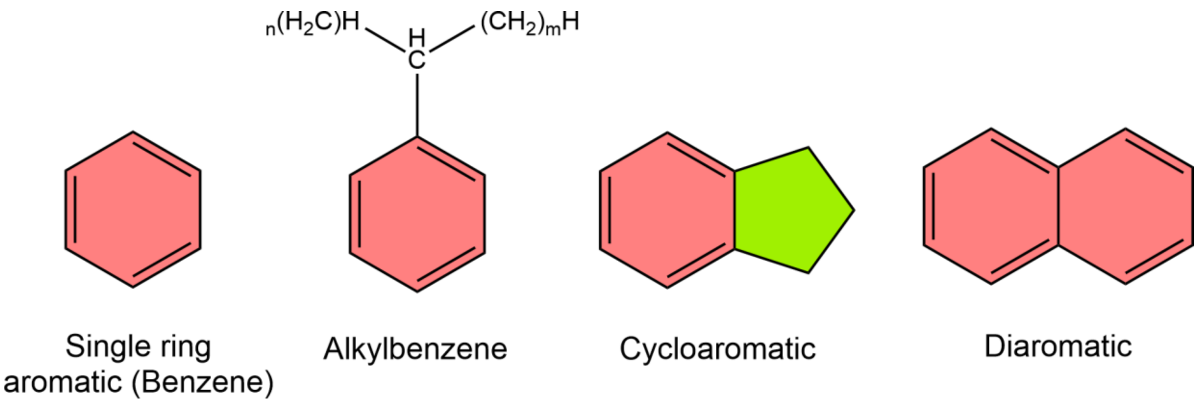


Figure 2.2: Examples of aromatics molecule types

A full list of the molecule classes and sizes measured by the University of Dayton Research Institute (UDRI) method for two dimensional gas chromatography (2DGC) [7] is presented in Appendix A (Table A.1) and shows the range of molecules that can typically be present in a conventional jet fuel. This illustrates the type and range of alkyl attachments which can be present. The three main classes of aromatics are alkylbenzenes, alkylnaphthalenes (aka naphthalenes) and cycloaromatics. It would be expected that a measurement of “total aromatics” by the standard methods shown in Table 2.3 would include all these molecules but “naphthalenes” measurement would only include the alkylnaphthalenes. Note that the paraffinic molecule information is also included for information only.

2.4. Aromatic measurement test methods

The current test methods are summarised in the Table 2.3 below. A brief description of these methods is provided in Appendix A.

Table 2.3: Currently used test methods for Aromatics speciation (further details in Appendix A)

Method	Title / description
Specification tests (limited classification of molecules)	
ASTM D1319	Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (FIA)
ASTM D1840	Test Method for Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry
ASTM D2425	Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

Method	Title / description
Specification tests (limited classification of molecules)	
ASTM D6379	Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection
ASTM D8305	Test Method for The Determination of Total Aromatic Hydrocarbons and Total Polynuclear Aromatic Hydrocarbons in Aviation Turbine Fuels and other Kerosene Range Fuels by Supercritical Fluid Chromatography
ASTM D8267	Test Method for Determination of Total Aromatic, Monoaromatic and Di- aromatic Content of Aviation Turbine Fuels Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection.
R&D tests (full classification of molecules)	
UDRI Method FC-M-101[1]	Flow Modulation GCXGC for Hydrocarbon Type Analysis of Conventional and Alternative Aviation Fuels

[1] [7]

As shown in Table 2.3, there are a wide range of methods to measure and characterise aromatics used by the industry in a range of applications. These vary from providing a single percentage number of total aromatic content which includes all species with at least one aromatic ring through to providing to complex two-dimensional gas chromatography i.e. 2DGC (also sometimes referred to as GCxGC) methods that provide detailed speciation of individual aromatics in terms of molecular weight, number of rings etc. In general, simple methods as applied to specification testing provide a single percentage, by mass or volume, as their role is to be relatively user friendly, quick and provide a simple number against a specification limit to demonstrate a batch of fuel meets the required specification and can be traded as Jet A/A-1. More complex methods which provide more granularity and speciation are not generally used for conventional fuels in service. These test methods are however used in the research and evaluation of novel fuels such as the ASTM D4054 process to evaluate new synthetic blend stocks which may be included in ASTM D7566 annexes, research studies on the impact of fuel composition on performance and/or “extended requirements” in synthetic fuel specification analysis. In this context, extended requirements mean additional testing during initial set up of production or during management of change of the process.

The test methods in use today have evolved from basic visual chromatographic manual methods of species separation e.g. ASTM D1319 to instrumental based methods e.g. D6379. All (apart from the naphthalenes method) rely on the separation of the aromatics by various chromatographic means and then detection by appropriate technologies.

It is also important to note that many of the instrumental methods, configured for standard specification testing, have defined algorithms that calculate a single result for total aromatics and/or a single result for single/multi-ring aromatics. These algorithms are often designed to give results that have parity with the previous methods that they replace so preserving the status quo. However, some of these methods could be configured to provide more in-depth detail of the aromatic species if required.

The following review provides an overview of the range of test methods in use, and by understanding their capabilities and limitations, provides a good grounding for understanding what information is available on aromatics in fuel for both a historic review of aromatic impact on fuel behaviour and an understanding of what data could be available in the future based on the capability of current test methodology. Further, understanding of capability and limitations of these methods provides an understanding of what data could be gathered and what revised controls would be feasible.

Note that in some cases there are equivalent methods to ASTM which are used in other specifications such as Def Stan 91-091 which are identified as “IP XXX”.

2.5. Test method applications

The measurement of aromatics is an integral part of any fuel analysis from early evaluation and development through to standard specification tests of every batch. Table 2.4 provides an overview of the commonly used aromatics measurement methods within specific test applications. Note that all ASTM methods are contained in the specifications and methods manual, published annually [8].

Table 2.4 Example of Specification Test Methodology

Specification	Test methodology and limits
Def Stan 91-091 / ASTM D1655[1]	**Aromatics** (1) Percent by volume, or max 25 - D1319 IP 156C or D8267 or D8305D (2) Percent by volume max 26.5 - D6379/IP 436
	One of the following requirements shall be met: (1) Smoke point min 25.0 mm - D1322/IP 598, or, (2) Smoke point min 18.0 mm - D1322/IP 598 and Naphthalenes, percent by volume max 3.0 - D1840 or D8305R
ASTM D7566[2]	**Final Blend:** **Aromatics: One of the following requirements shall be met:** (1) Aromatics, volume percent Max 25 - D1319 or IP 156C or D8305X (2) Aromatics, volume percent Max 26.5 - D6379/IP 436
	Neat SPK blendstock (e.g. SPK to Annex 1 or 2) Hydrocarbon composition Cycloparaffins, mass % Max 15 - D2425 Aromatics, mass % Max 0.5 - D2425 Paraffins, mass % report - D2425
ASTM D4054[3]	Aromatics - D1319 D6379 HC Speciation - UDR FC-M-101[4]

[1] [9], [2] [4], [3] [10], [4] [7]

Prescreening work

Deutsches Zentrum für Luft- und Raumfahrt (DLR), as part of the Jetscreen EU project (https://cordis.europa.eu/project/id/723525) [11] and Washington State University programme [12] have developed prescreening technologies that include the use of their own versions of 2DGC. Each uses bespoke 2DGC methods. Washington State has done some cross correlation with UDRI [7] and have stated that they get very similar results for aromatics content.

Prescreening work carried out at DLR and Washington State University use their respective version of 2DGC to analyse jet fuels and blendstocks to predict fuel properties including Yield Sooting Index (YSI), amongst others [13] in the early stage of candidate fuel development when only small volumes of sample are available using machine learning tools [2]. This 2DGC data may also be augmented by limited small scale laboratory tests. Whilst the techniques are similar, they would not necessarily get exactly the same results as each other or the current industry reference (UDRI). For critical ASTM evaluation work this is important to use the UDRI reference method. For prescreening research studies the differences are most likely not significant or critical. Work is ongoing across the industry and particularly being coordinated by the US, UK and EU Clearing Houses to provide more facilities that can carry out this 2DGC analysis to the same standard.

2.6. Common features of ASTM test methods

The methods define all the equipment and methodology for completing the measurements in a rigorous and high level of detail. For this study some key common features are discussed below.

Definition of scope

Each specification defines the scope of fuel types that can be analysed by the method with assurance that the precision will be within stated limits, and any interference compounds are cited. Scope in the case of aromatics often includes the max and min aromatics levels. Note that some of the older methods are not capable of measuring the very low levels in neat SPK type products. This is not currently an issue as all current drop-in fuels have at least 8% aromatics, but work is ongoing through the ASTM Aviation Fuel sub committees to either lower this level in conventional fuels or ultimately allow zero aromatics.

Precision and bias

Each of the above methods have an associated precision and bias statement apart from UDRI Method FC-M-101 [7] which by its nature is not sufficiently widely available at different locations to enable the analysis to determine this data. In summary:

Repeatability—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the stated values only in one case in twenty.

Reproducibility—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the stated values only in one case in twenty.

Bias—is not always stated but may refer to reference materials or reference to previous methods that have provided the industry with an accepted baseline e.g. some more recent instrumental methods have a bias statement using ASTM D1319 and/or D1840 as the established industry reference.

It is important to bear the repeatability, reproducibility, and bias of these methods in mind when using these methods for specification control. However, for this study it is sufficient to note that results from any of the methods in Table 2.3 (excluding UDRI Method FC-M-101) have sufficient precision to be used for specification testing so will be adequate for data in this study or indeed could be to control aromatics at different levels in the future.

2.7. Future developments

The industry is currently working on two types of jet fuel for the future.

Firstly, in the nearer term there is a 100% SAF that is a drop-in that is compatible with all current aircraft in service. This will comprise a blend of SPK and synthetic aromatics. The composition of these synthetic aromatics will almost certainly be different and most likely a less complex and diverse mixture than those present in conventional fuels. This may require different ways of defining and limiting concentration since say 10% of conventional aromatics will be different in behaviour to 10% synthetic aromatics.

Secondly, in the longer term is the proposal for a 100% Sustainable Aviation Fuel that is a non drop in (i.e. not blended with conventional fossil jet fuel and containing below 8% aromatics). This will be based on an SPK but with some optimisation and changes in properties to maximise the benefits. As such these will be essentially (as an initial target) zero aromatics but with a practical limit of 0.5%, so methods capable of measuring down at this level will need to be made more common.

Work is always ongoing to improve test methodology. It is likely that analytical methods for R&D and novel fuel evaluation will increase in capability but with attendant complexity e.g. improvements in 2DGC (see above). However, the use of such methods for specification testing is not likely as R&D capabilities are expensive to run and require significant levels of training to operate successfully. The intention of specification tests is completely counter to these limitations of R&D tests, as they are designed to be relatively simple to operate and interpret, are widely available around the globe and are relatively cheap to use. This means that evaluation capability of analysing and characterising aromatics in R&D type work will always be ahead of the capability that could be called on to measure and control aromatics in everyday fuel batch testing.

2.8. Discussion

Aviation fuel is produced to standardised, internationally agreed specifications[2] and is commonly known as Jet A/A-1. These specifications allow national and international air transport to take place, aircraft, engines and fuel supply systems to be designed, manufactured and certified to operate with a common set of fuel requirements. The specifications are in essence, a compromise between the cost of fuel production and the cost of operation using these fuels. Any change to the specification to reduce the environmental impact of any fuel must be carefully considered and the implications of any change thoroughly investigated.

Conventional fuel specification type tests as defined in Def Stan 91-091, ASTM D1655 (or equivalents) are likely to be widely available and data produced by these methods will be available from test certificates and surveys thereof. There has been a general trend in the industry to move from the "manual" type methods such as ASTM D1319 and ASTM D1840 to the equivalent chromatographic instrumental methods such as D6379 or D8305. Whilst some care has to be taken regarding the method used, and if instrumental based, if there is a bias when comparing data. The relative prevalence of the manual vs instrumental methods is unknown, but each type gives comparable results, with due cognisance of biases.

These same methods are also used in ASTM D7566 (synthetic blends) for the final blend assessment to be in parity with ASTM D1655. Note that to be able to measure at the very low levels required for the neat blendstocks (synthetic paraffinic kerosene), ASTM D2425 is used. It is generally accepted that D2425 is a

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[2] DEF STAN 91-091 and ASTM D1655 in most of the world. Also, Chinese Fuel No. 1 and No. 2 and Russian TS-1 amongst others.

difficult method to operate and will be replaced when a suitable alternative is available, as shown in Table 2.4.

As regards this study, the key strength of these methods is that they are widely available and in use so data is easily accessed such that levels in current supplies could be monitored given that every batch of jet fuel is tested before dispatch. And, if this study considers the potential to change the limits of aromatics (single and/or total and/or multi-ring) then these methods could be stipulated as available for everyday batch control. They generally meet the key criteria for specification type tests that are used in production and control within the fuel refinery and delivery system i.e. they have adequate precision, relatively easy and quick to carry out and do not require highly specialised laboratories or staff. Further, instrumental methods have removed any subjectivity.

The methods listed in Table 2.3, have, to date, generally delivered and continue to deliver the controls on aromatics and consequent fuel performance such that fuels have remained within defined bounds. The key limitation of all the standardised methods in Table 2.3 is that, by design, they only give broad class data i.e. concentration of total aromatics, single-ring aromatics and/or multi-ring aromatics. These therefore give no insight into the composition within these broad classes such as molecular type and carbon number which would be useful for studies into the impact of aromatics on other performance properties, formation of smoke/particulate and contrails. These are therefore a somewhat "blunt instrument" for more detailed studies, however they remain the most widely used methods and can be used to explore the problem space. These methods are also of limited use for new synthetic blendstocks which may have very different molecular types and distributions from conventional fuels.

For novel fuel evaluation and prescreening aromatic types by 2DGC is now the industry standard method. Pre-screeners (DLR and Washington State) have their own versions which probably give similar results to the industry standard method. The industry standard for fuel evaluation to ASTM D4054 requirements is currently carried by the UDRI to internal method UDRI Method FC-M-101. Whilst this gives much greater insight into detailed fuel composition of all hydrocarbon types it is a bespoke method, and at this point in time, is only available from UDRI. Therefore, the availability of data is limited to detailed fuel property surveys such as the CRC world fuels survey and associated reports [14], novel fuel evaluations and R&D on the impact of aromatics on other fuel properties. The prescreening methodology also allows the prediction of some key properties without the requirement to carry out actual measurements [2]. However, the predictive capability is still under development and no real precision data is available, so this methodology remains only suitable for R&D type work.

Currently the capability to carry out 2DGC to recognised standards is limited to the University Dayton (US Clearing House). However, it is likely that there will be several more facilities which are able to do this method including the SAF-IC laboratories based at Sheffield primarily serving the UK. Further, Trinity College, Dublin as part of the EU SAF Clearing House organisation is planning to set up 2DGC systems. Note, as discussed earlier, these two facilities are in the process of setting up and working with UDRI to be able to provide results that are the same within experimental error. The 2 prescreeners may at some point work towards parity with these laboratories. Giving a total of at least 5 2DGC facilities in the foreseeable future.

Given the high cost of 2DGC equipment (in the order of several hundred thousands of pounds) and the complexity of operation, and at this time there is no ASTM method, it is unlikely that this method will be in common use in the foreseeable future.

There are a number of potential options for implementation of a reduced aromatic content of jet fuel including:

1. Fuel Supplier Options (aromatic mandate)
2. Reduce the percentage of total sulphur (by mass), as measured by the standardised tests already in use. This has been investigated in a limited number of studies.
3. Reduce the percentage of total aromatics (by volume) that fuel suppliers can include in jet fuels, as measured by the standardised tests already in use. This may limit the ability to blend fuel with SAF.
4. Reduce the di-aromatic (or naphthalene) limit (currently at 3% by volume), as measured by the standardised tests already in use. Some limited assessment of this approach has been made in the literature.
5. Increase the smoke point limit (currently at 25mm), as measured by the standardised tests already in use. This could be a useful “catch all” performance parameter.
6. A combination of the above

2.9. Research gaps

Some of the instrumental methods used in the specification could be adapted to give a more detailed composition of the aromatics in fuel. However, this is not currently seen as a priority within the specification authorities to take on such work. This may be required if an identification of specific aromatic molecules is required in future beyond a catch all “total aromatics” and “naphthalenes” as is currently in the specification.

It is also notable that many of these methods were not designed for, nor does the industry have significant experience of, measuring aromatics at very low levels, below 8% and further studies are required to assess the precision of these methods at very low concentrations of aromatics in fuels.

2.10. Conclusions

[Note, confidence statements below are preliminary and are subject to further discussion and feedback]

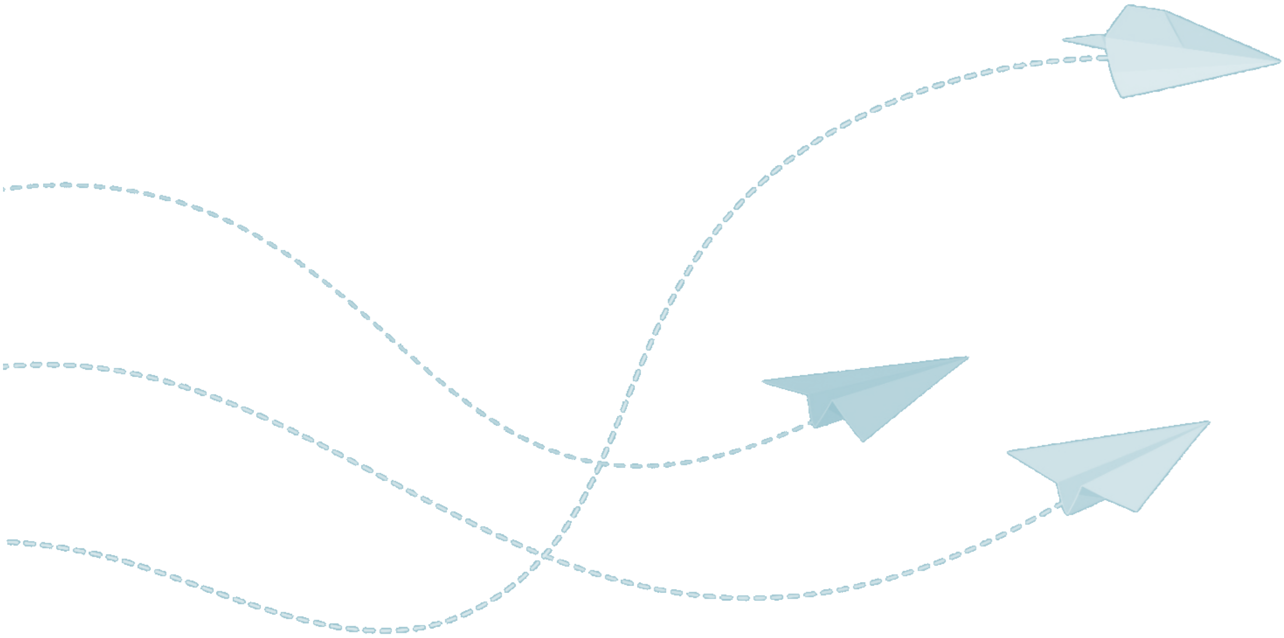
1. It is not advisable to consider measured %hydrogen content as a direct substitution for the measurement of specific classes of components in the fuel, such as “aromatic content” which covers the classes containing at least one aromatic ring. For real fuels, made up of a range of structures and carbon numbers the same %H can be achieved by many different combinations of composition which can result in a range of property values and performance characteristics. **(high confidence)**
2. Standard specification type aromatics measurement tests provide a quick and easy way to measure aromatics and are in daily use to test and certify production batches of fuel and/or carry out quality assurance downstream so are widely available. **(high confidence)**
3. In their current form these standard tests only provide simple information in terms of the concentration of broad categories of aromatics defined as single-ring aromatics, multi- ring aromatics and/or total aromatics. Note that these measures and limits are also controlled alongside smoke point as an additional evaluation of combustion properties. **(high confidence)**

4. Any proposal to drive the industry to change the type or level of aromatics in everyday supplies is likely to be limited to the use of standard methods already referenced in the fuel specifications and so only minimum and maximum values can be altered without further development and investment in specific measurement methods. **(high confidence)**

5. 2DGC is a much more recent and advanced methodology which provides much more information on the composition within these broad categories. This is an invaluable tool for novel fuel evaluation and R&D around the impact of aromatics on other properties and many reference documents from ASTM new synthetic fuel evaluations are available with 2DGC data. This dataset is growing as more candidate fuels are evaluated for inclusion in the fuel specifications. **(high confidence)**

6. It is not recommended to drive the industry to change by requiring the widespread use of advanced 2DGC equipment. It is unlikely that 2DGC equipment will be available widely in the near future and certainly not available for fuel batch production testing. At this time there are only a handful of facilities that can carry out 2DGC and the only laboratory that could currently carry out the UDRI method is UDRI themselves. Others, such as the UK and EU SAF Clearing House are currently working on providing such a service. **(high confidence)**

7. Some of the existing instrumental methods as used in specification testing may be capable of more detailed speciation but no significant efforts are being made to develop and standardise to operate in this more detailed manner at this time. **(medium confidence)**



3. Fuel production, composition and properties

Summary

This chapter provides more detail on fuel production methods, and how this relates to the sources and types of aromatic compounds in jet fuel. Aromatic compounds are a complex mixture of different types, built upon single and multiple rings of carbon atoms, that have multiple possibilities for side chains of carbon and hydrogen, along with ‘trace compounds’ of sulphur, nitrogen, and metals. The detailed chemical composition is initially dependent upon the source of the crude oil, and is then modified at the refinery, as necessary, by a process known as ‘hydrotreatment’, whereby impurities are substituted and removed by hydrogen gas via a catalyst. Hydrotreatment and hydrocracking are outlined in the context of UK and global jet fuel production facilities. The associated costs of these processes are summarised in the context of any requirement to increase capacity, in order to reduce the aromatic content of jet fuel. If aromatic reduction of jet fuel is required, hydrogen production will need to be increased, the vast majority of which is currently ‘grey’ (fossil-based), resulting in extra associated CO_2 emissions. The specification of jet fuel controls the physical and performance properties of fuel to internationally agreed standards which are relatively easy and quick to measure as part of a global fuel supply system. The specification does not however specify the exact chemical composition of the fuel. Jet fuel is a fungible, traded commodity. Therefore, the detailed composition by source (of the crude oil), or an individual batch, of fuel is generally either not known or documented, and only detailed specific studies provide such information. There is an inverse correlation between total fuel hydrogen content and aromatic content – i.e. as aromatic content decreases, hydrogen content increases, and vice versa – but the scatter in the data is large, meaning that as a proxy, hydrogen content is a poor metric for potentially regulating aromatic content. Increasing hydrotreatment is shown to be a non-linear function of the production cost/energy requirements, requiring greater costs/energy for more severe (effective) reduction of aromatics. Initial evidence suggests that removing specific aromatics such as naphthalene (which is associated with soot emissions) will have an energy and therefore CO_2 cost. Reducing aromatics will limit the blending capability of conventional fuels with SAF, since there is a safety-based minimum requirement of 8% total aromatics for semi synthetic jet fuels. In summary, hydrotreating will require extra hydrogen sources (which currently are ‘grey’), will increase energy density of the fuel with a small reduction in CO_2 emissions, the hydrotreatment process itself will incur extra energy and CO_2 at the refinery, and the fuel with have greater emissions of water vapour (a greenhouse gas). These interplays are complex and make decision making on whether there is a net environmental benefit highly complex.

3.1. Source and type of aromatics in jet fuel

The final chemical composition of Jet A/A-1 fuel is a combination of the original crude oil composition and the refining technologies used to convert it. Aromatics in jet fuel are complex and closely related to the crude used at the refinery [15]. Figure 3.1 outlines a ternary composition diagram for global crude oils to illustrate the complexity of the origin of the aromatics [16]. Typically, crude oils are split into three compound classes (1) Saturated Hydrocarbons (paraffins, bottom left corner indicates 100% content in crude), (2) Aromatics (top corner indicates 100% content in crude) and (3) Asphaltenes (cycloalkanes, bottom right corner indicates 100% content in crude). The dots in the diagram indicate crude oil compositions from around the world where they can range from close to zero to 60% aromatics. Crudes historically used by refineries in the UK and EU from the North Sea ("Normal Crude" e.g. Brent Crude) have an aromatic content between 20-40%. As North Sea crude oil production is dwindling, alternative crudes with higher aromatic and asphaltene content are being used adding a further complexity to the aromatic composition and a greater need for hydrotreatment.

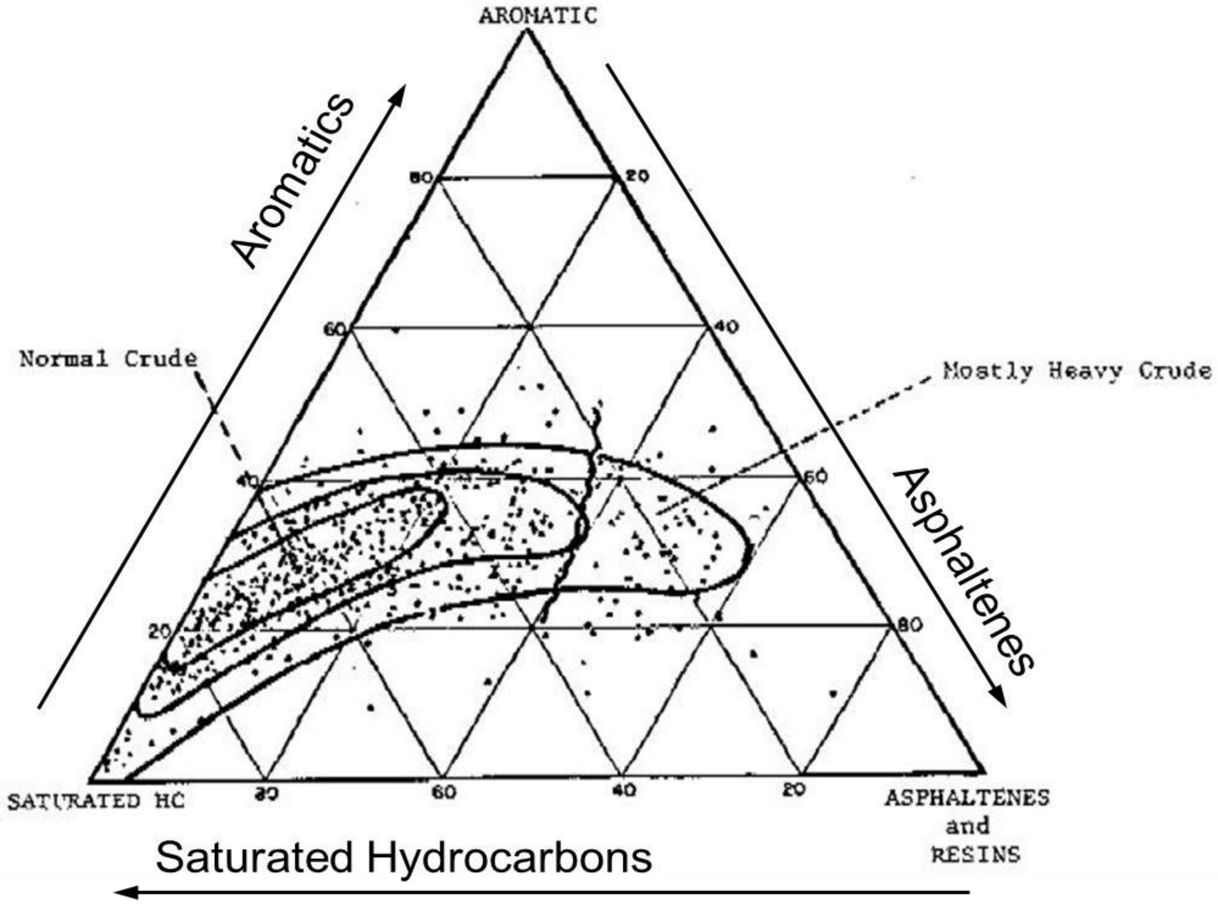


Figure 3.1: Ternary diagram of global crude oils [16]

An added difficulty with increasing aromatics in the crude oil is the increasing presence of heteroatomic compounds, i.e. other elements than carbon and hydrogen [17]. Figure 3.2 illustrates this issue in terms of nitrogen and sulphur. Brent Crude is a sweet crude with a high API Gravity (i.e. low density) of around 35 to 40 and low Sulphur (<0.5 wt%) and nitrogen (<0.1wt%). The crude of highest proven reserves in the world (Venezuela, 300 billion barrels) can have API below 15 and sulphur contents up towards 5wt% [17]. Progressive environmental legislation has set very low limits for a range of transportation, shipping, heating and aviation fuels, such as 0.3 %mass for Jet A/A-1 by ASTM D6155 or Defence Standard (DEF STAN) 91-091 [18] mandating removal of sulphur and nitrogen containing compounds during refining. This removal is normally achieved through treatment and/or cracking with hydrogen and might affect the nature of the aromatics since N and S are normally associated with aromatic complexes.

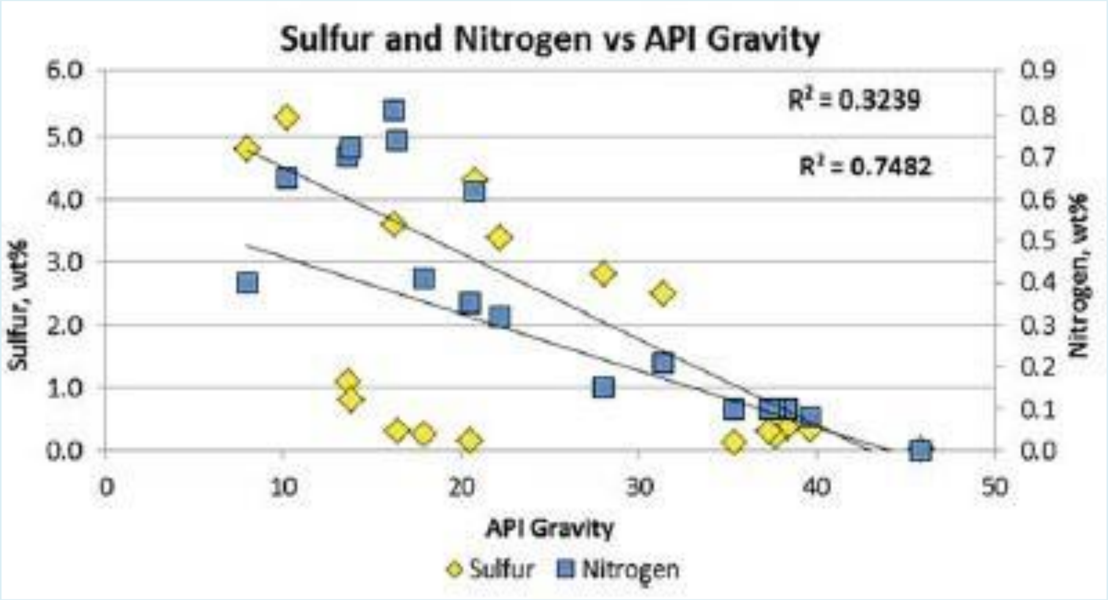


Figure 3.2: Typical spread of sulphur and nitrogen in globally traded crudes [17]

3.2. The need for hydrotreatment

Figure 3.3 shows the most common aromatic complexes associated with N and S and other heteroatoms, such as oxygen and nickel [19]. The reaction with hydrogen aims to remove the heteroatom from the aromatic complex and create a gas that can be dealt with separately. E.g. thiophenes (liquid) can be reacted with H_2 (gas) to form a paraffin (liquid hydrocarbon only) and H_2S (gas). Here the hydrotreatment both removed the heteroatom (S) and the aromatic compounds that can affect many of the final fuel properties [20].

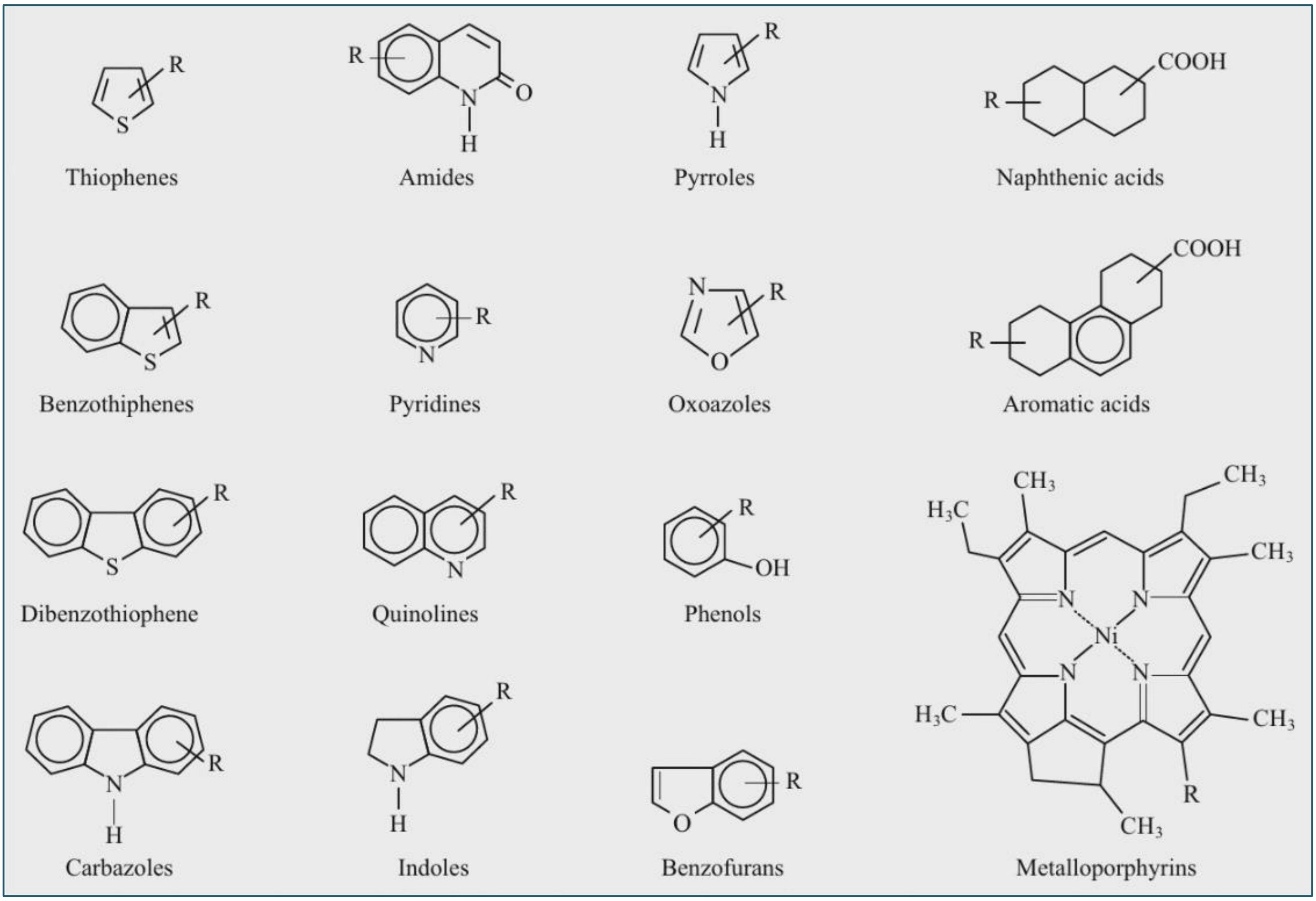


Figure 3.3: Most common aromatic complexes with associated Nitrogen, Sulphur and other heteroatoms such as oxygen and nickel [19]

Hence, hydrotreatment is a strong tool for refiners to regulate heteroatoms, which is generally beneficial for the jet fuel fraction, as well as reducing the aromatic content. Figure 3.4 lists the most common aromatic (single and multi-ring) compounds found in different crudes where the - R indicates alkyl substitutions, as described in Chapter 2. These are normally paraffinic attachments with carbon numbers ranging from 1 to over 10. Therefore, a compound classified as aromatic can be >50 wt% paraffinic in nature which adds to the complexity of the discussion on aromatics in jet fuel [21] (as described in Chapter 2). During hydrotreatment, the aromatic ring is normally regarded as converting to its cycloalkane form, e.g. alkylbenzene converts to alkylcyclohexane. However, removal of alkyl side chain and/or ring opening might also take place depending on the nature of the processing in the refinery.

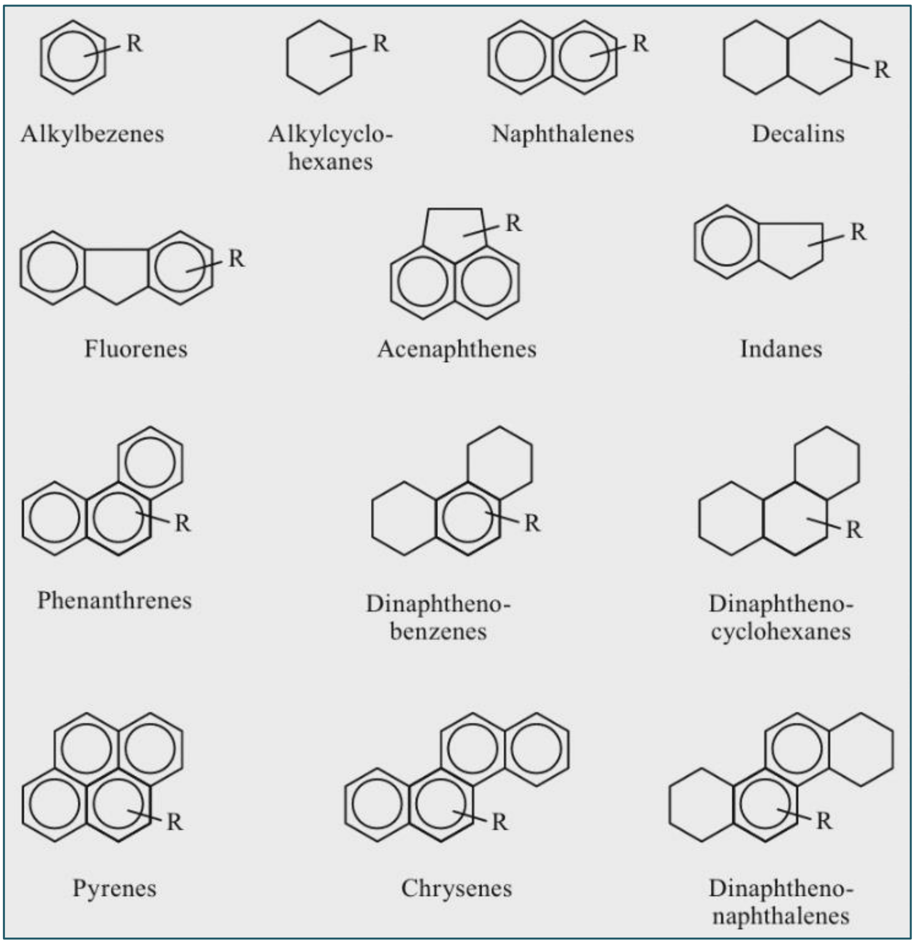


Figure 3.4: Most common aromatic compounds found in different crudes where the -R indicates alkyl substitutions of paraffinic attachments with carbon numbers ranging from 1 to over 10 [19]

3.3. Jet fuel processing

Processing of crude oil is a complex process with a very small economic margin which mandates large refineries. In the UK there are currently six refineries of which Fawley is the largest, processing 270,000 barrels of crude each day and has a direct jet fuel pipeline to Heathrow [22]. The UK demand for Jet A-1 was around 3.8% of the global consumption of Jet A/A-1 in 2017. The UK has a relatively low domestic production of Jet A/A-1, in 2017, 57% of Jet A-1 used in the UK was imported [23]. Figure 3.5 shows a common conversion refinery with several complex operations. There are a range of less complex refineries, such as hydroskimming and topping refineries, that are also used [19] and account for around 4% of all fuel produced globally [23]. There is a range of products from a refinery and it is important to highlight that kerosene (or jet fuel) might be a small fraction of the output depending on the market conditions. Hence, jet fuel is normally “made” by mixing several streams from the refinery. Figure 3.6 shows the refinery processes used in the production of Jet A/A-1 around the globe. The main ones are indicated in the light blue boxes marked “4” in Figure 3.6.

The distribution of Jet A-1 from different refining routes in 2017 is shown in Table 3.1 along with global and regional values. Around 37% of Jet A/A-1 produced globally and 70% of the Jet A-1 produced in the UK is straight run fuel from atmospheric distillation (CDU) which is the simplest method for producing Jet A/A-1 [23]. This clearly shows the refining capacity in the UK is heavily biased to the refining of crude oil from the North Sea, which as mentioned earlier in the Chapter has relatively low sulphur and aromatic content, requiring less hydrotreating.

Hydrotreating is typically used to remove oxygen, sulphur and other heteroatoms from petroleum products and involves the pumping of kerosene reactants from atmospheric distillation combined with hydrogen gas through a reactive bed at pressure and temperature. The catalyst in the reactive bed is usually Cobalt or

Molybdenum on Alumina. It produces a byproduct of H_2S gas. Refinery hydrotreating is often sub classified into kerosene hydrotreatment (KHT) and diesel hydrotreatment (DHT)

A Distillate Hydrocracking Unit (DHCU) is a more energy intensive process and is typically used to break up more complex hydrocarbon molecules in the form of residues and waxes into structures more like those in Table 2.1 (converting high boiling point compounds into low boiling point compounds). As with hydrotreating, the reactants are combined with hydrogen in a catalytic bed of Nickel, Platinum or Palladium on Clay, Alumina, or Silica Alumina at higher temperature and pressures than the hydrotreating process.

Table 3.1: Proportion of Jet A/A-1 from refinery sources [23]

	CDU Jet (%)	KHT Jet (%)	DHT Jet (%)	DHCU Jet (%)
Global	37.2	25.6	21.2	16.0
EU + Russia	26.6	19.5	37.1	16.8
UK	69.9	1.2	20.9	8.0

* A further breakdown by nation state is available in this reference supporting material

Also note that hydrogen (white box labelled “1”) is recovered from various processes and used during hydrotreating (HT) and hydrocracking which might avoid the cost of a separate hydrogen production unit (currently hydrogen production is predominantly through Steam Methane Refining (SMR), see Section 3.5). Overall, the refinery is trying to maximise profit on the different streams as guided by the market conditions and output product slate, and mixing is therefore a common approach to achieve jet fuels that meet standards (Figure 3.6).

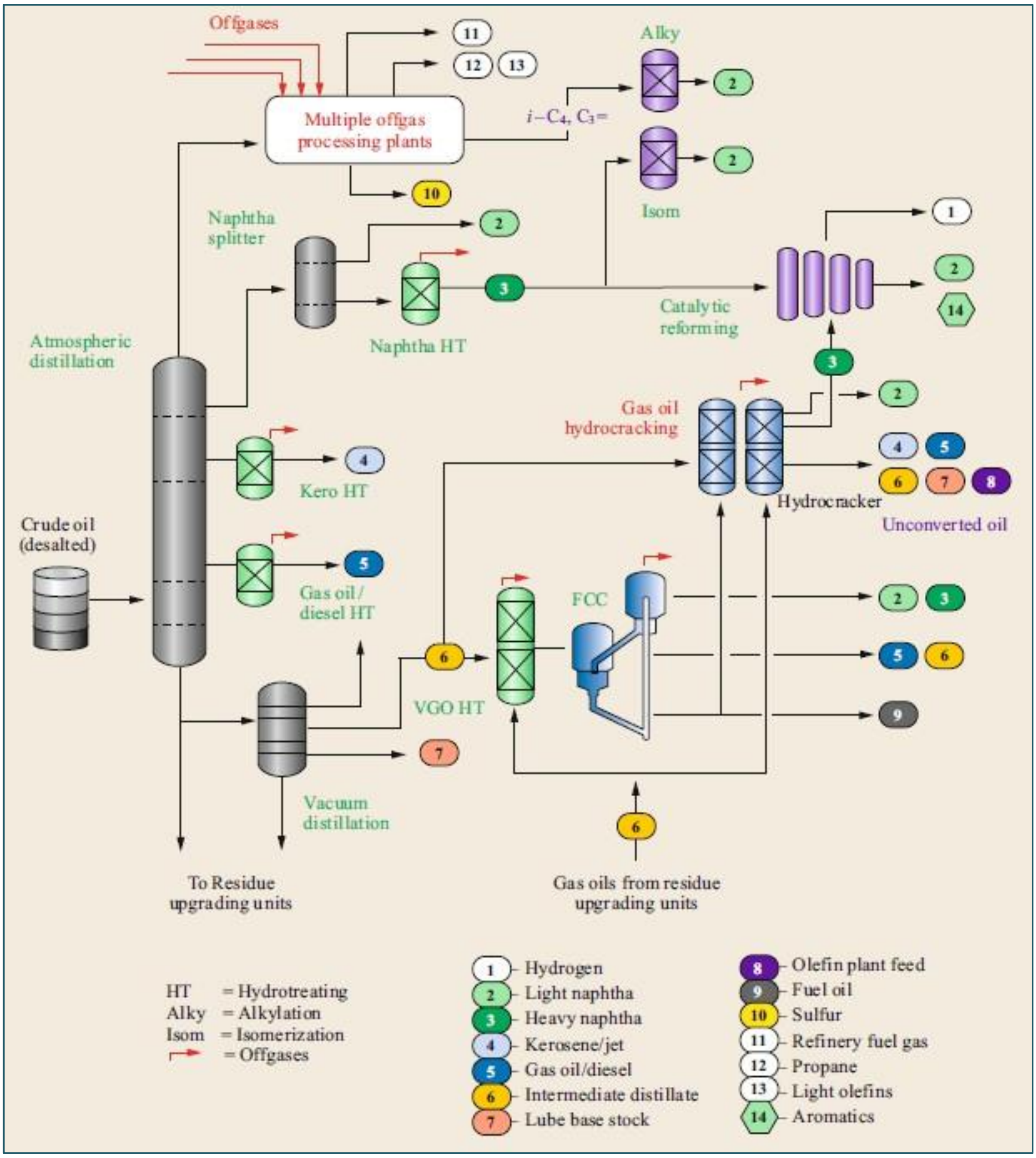


Figure 3.5. Common conversion refinery with several complex operation [19]

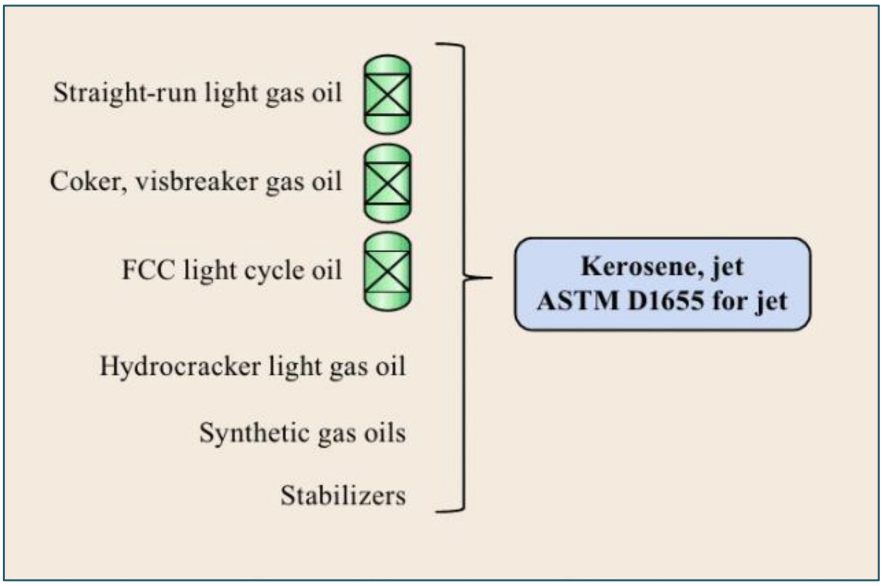


Figure 3.6: Mixing approach to achieve jet fuel that meet standards [19]

The volumetric composition of Jet A/A-1 from different production processes is broken down more explicitly in Figure 3.7.

The use of mixing different refinery streams adds to the complexity of characterising the aromatics in jet fuel as shown in Figure 3.7 [17]. In DEFSTAN 91-091 and ASTM D1655, the kerosene boiling point range is given by ASTM 86 stipulating that maximum 10wt% should be lost below 205°C and 100% should be vaporised at 300°C which is indicated grey box labelled “Kero (Jet)”. In this boiling point range, there are various compounds containing one, two and more aromatic rings. Hence, refineries will meet standards by having aromatics below 25% mass (ASTM D1319) where two+ rings (di-aromatics) are limited to 3% mass. More advanced measurement methods are now available on an R&D scale as discussed in Chapter 2.

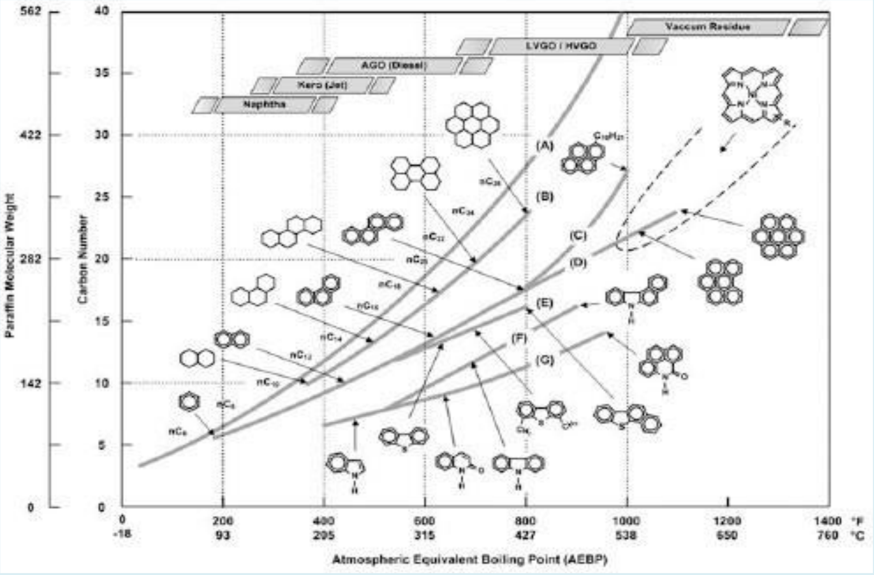


Figure 3.7 Complexity of characterising the aromatics in jet fuel [17] showing the range of aromatic compounds in the kero(jet) range compared to other refinery products

3.4. Hydrocracking and related aromatic control technologies

Currently, the readjustment of aromatics in aviation fuels are controlled by mixing (see Section 3.3) and any change in the aromatic fraction due to hydrocracking (HC) or hydrotreatment (HT) is an indirect consequence of focus on removal of heteroatoms such as sulphur to create lower sulphur products (see Section 3.2). Assuming that low aromatic crudes (sweet crudes) are progressively being replaced by higher aromatic crudes (sour crudes) in the UK, the increased use of HT/HC will be critical for refineries in the future as refineries will move to heavier and sour crudes. If aromatics as a whole or a specific aromatic fraction (such as multi-ring aromatics) would be further regulated for crude oil refiners, there are two strategies currently identified (1) increased use of hydrotreatment and/or hydrocracking (HT/HC) or (2) selective removal using extractive distillation. The former strategy is broad based and does not selectively target di- aromatics while the potential use of extractive distillation could specifically remove di-aromatics (not currently commercially available). Table 3.2 compares some of the issues with these two options, including estimates of the cost of operation of these technologies from the limited literature available [24].

The removal of naphthalenes by hydrotreatment would increase the price of Jet A/A-1 by +4.7 US cents/litre and by +3.1 cents/litre for extractive distillation. This can be compared with the cost of sulphur removal which is estimated to be around 1.4-2.1 US cents/litre [24].

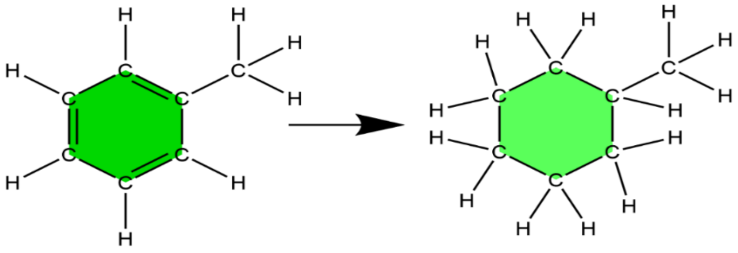
Table 3.2 Comparison of aromatic removal strategies for refineries (adapted from [24] and [25])

	Approach 1 Broad based, commercially available Hydrocracking (HC) / Hydrotreatment (HT)	Approach 2 Potentially selective di-aromatic removal by using Extractive Distillation
Compounds targeted	Broad based and non-selective saturation of aromatics	Compound specific. e.g. used for producing benzene, toluene and xylene (BTX) for the chemical industry.
Process established	Yes. However, increased use will most likely require separate hydrogen production.	Not for general fuel use. Most commercial extractive distillation processes focus on value-adding of particular compounds, such as active ingredients for pharmaceuticals.
Adding value	Great potential for adding carbon free hydrogen to fossil fuels for gradual introduction of low carbon alternatives.	Uncertain. Selective removal of naphthalene (i.e. multi ring aromatics) will create a stream of concentrated polyaromatic hydrocarbons (PAHs) that arguably has a negative value.
Mean market cost change for Jet A/A-1[1]	+14%	+9%

[1] [24]

Hydrocracking (HC) /Hydrotreatment (HT) are generally broad based and non-selective saturation of aromatics as illustrated through Figure 3.10. This can also be considered as a reduction in the HD from 4 to 1 through the process of hydrotreatment (where a HD of 0 represents a fully saturated molecule, which is the easiest to combust). The corresponding changes in fuel characteristics are presented in Table 3.3. Saturation of aromatics creates several challenges. Firstly, it reduces the fuel density. Secondly, it might increase the freezing point, lower the flash point and decrease the autoxidation (storage stability) characteristics of the aviation fuel [21]; [26]. The implication of these changes will be discussed in a later section of this Chapter and in Chapter 3. Whilst removal of heteroatoms has some desirable effects such as improved thermal stability, it may also alter other bulk and trace dependent properties such as lubricity and/or storage stability. These side effects have to be considered by the refiner to ensure the final fuel is fit for purpose and may require further blending and/or consideration of use of additives (this is discussed further in Chapter 4). Thirdly, if extra hydrogen is needed at the refinery there will be related process emissions (additional CO_2 and NO_x) if green hydrogen is not used.

As an illustrative example the following shows how hydrotreatment can modify toluene. Note this is provided to demonstrate the principle on a simple, relatively small alkyl aromatic. Toluene would not usually be found in jet fuel due to its volatility being outside the accepted range.



Toluene (HD = 4) Methylcyclohexane (HD = 1)

Figure 3.10: Saturation of toluene using hydrogen

Table 3.3: Change in fuel characteristics by saturation of toluene into methylcyclohexane using hydrogen

	Toluene	Methylcyclohexane
Density, kg/m^3	867	770
Volumetric calorific value, GJ/m^3	35.2	33.7
Mass based calorific value GJ/kg	40.60	43.77
Chemical formula	C_7H_8	C7H14
Combustion products	7 CO_2 + 4 H_2O	7 CO_2 + 7 H_2O
Comments	Helps increase volumetric fuel density that needs to be between 775-840 (ASTM D1298) Greatly compensates for increased paraffinic SAF fraction with typical volumetric fuel density below 770 kg/m^3	Lower than fuel density specification that needs to be between 775-840 (ASTM D1298); - Requires larger fuel tank (>4%) compared to toluene; - Requires more air for combustion (>17%) leading to more energy used for the compressor. - Emits more water (>75%) in the stratosphere.

Globally, crude oil feedstock varies in composition, not only in aromatic content but also in Sulphur content and other key variables which alter the processes necessary to generate Jet fuel from a given crude [27]. Hydroprocessing and hydrocracking are both processes capable of converting aromatics to cyclo-alkanes as described above [28]. This is achieved by addition of hydrogen to crude oil vacuum distillates and a variety of other feedstocks at temperature and pressure over a catalyst bed and is a function of liquid hourly space velocity through the hydrocracking reactor. This process reduces the HD of the fuel.

Typical pilot plant hydrotreaters operate at high pressure (between 5 and 10MPa) and temperature (between 270 and 340°C). Commercial plants are often more highly optimised and increasing the reactor temperature is not an option due to the configuration of the refinery and the metallurgy of the catalyst bed [29].

Kittel et al. [30] show, at industrial scale, that the Jet A-1 yield of a Hydrocracking reactor reduced from 15 wt.% to 10 wt.% over a period of 173 days' time on stream. Over the same period, the aromatic content of the jet fuel produced increased from 13% by volume to 26% by volume due to catalyst deactivation. Kittel et al. [30] compare hydrocracking with hydroprocessing, showing that hydrocracked Jet A-1 contains a narrower cut, predominantly C10-C12, with low n-alkane content in comparison to hydrotreated Jet A-1 which contains C10-C13 with a much larger fraction of n-alkanes.

Vivas-Báez et al. [31] show that conversion of aromatics to cyclo-alkanes is a function of catalyst time on stream, temperature and aromatic content. Furthermore, they find that catalyst deactivation occurs as a function of time on stream and aromatic content [31]. Other compounds also serve to accelerate the deactivation process, such as organic nitrogen compounds found in crude derived vacuum gas oil (VGO)

Hussein et al. [32] show that sulphur content and aromatic content of hydrotreated kerosene processes are a function of, temperature (non-linear), pressure (non-linear) and liquid hourly space velocity (approximately linear) as well as the hydrogen to hydrocarbon ratio on pilot scale plants.

Furthermore, Kittel et al. [28] performed follow on work from the industrial scale testing shown in their earlier work (Kittel et al. [30]) using kerosene from the late stage of the previous experiment with approximately 22 wt.% aromatic content as a feedstock for a small (laboratory) scale through-flow hydrocracking unit. Tests were performed with a commercially available catalyst (3.3 wt.% Ni, 19.6wt.% Mo, sAl2O3). The catalyst was dried in hydrogen at 150°C and 0.5MPa prior to activation with straight run gas oil and dimethyl disulphide at weight hourly space velocity of 1h-1 (33g/s) and a hydrogen to feedstock ratio of 270 m^3/ m^3.

After catalyst preparation, Kittel et al. [28] processed straight run gas oil from prior large scale refinery experiments [30] with a mass flow rate 33g/hr and a hydrogen to feedstock volume ratio of 370:1. Hydrocracking was carried out at pressures of 3MPa and 6MPa were tested at temperatures between 290°C and 350 °C for a duration of 4 hours sampling generating a total kerosene sample of 120g per test. These conditions represented the extremities of processing in typical industrial hydrocracking units. Kittel et al. [28] find that it is possible to reduce Jet fuel aromatic content from ~22 wt.% to 3 wt.% at 6 MPa and reactor temperatures of 330 °C, the final product contained 60-70 wt.% cyclo-alkanes and 20-25 wt.% i-alkanes. The kerosene H/C ratio increased from 1.89 to 1.98 during hydrocracking. Clearly, for limited experiment

duration and scale available, this achievement represents a significant reduction in kerosene aromatic content. Severe hydrocracking currently represents an opportunity which should be studied at increasing scales as a proof of concept for jet fuel to determine the validity of this technology for use at scale. It is recommended that experiments should first be carried out at pilot scale with a variety of industrially available catalysts and a range of temperatures over long durations to determine the suitability of catalysts and rate of catalyst deactivation during screening tests to de-risk costly industrial scale testing. There are a limited number of facilities capable of this scale of research activity available in Europe and have been used in previous studies of sulphur removal [29] and successive hydrotreatment [11].

Kittel et al. [30] find that conventional kerosene can be hydrocracked using catalysts resulting in the conversion by hydrogenation of aromatic compounds to cycloalkanes. This can be achieved by a number of different catalysts to varying degrees of effectiveness to reduce the aromatic content of kerosene cuts to meet Jet fuel specification.

Table 3.4 presents available data from the literature which reports the hydrogen required per unit feedstock to the hydrotreating process to achieve increasing levels of compound removal through hydrotreatment and hydrocracking. These results are reported for specific crudes and the variance in the numbers may be a function of the varying levels of aromatics observed, however it provides some indication of the increasing hydrogen requirement as the severity of hydrotreatment or hydrocracking increases. This hydrogen demand is one of the main drivers of the cost and GHG impact of these processes.

Table 3.4: Reported hydrogen requirements for the removal of particular compounds

	Total Sulphur (ppm)	Total Aromatics (%)	Naphthalenes (di-aromatics) (%)	H_2 requirement (kg/tonne product)
Study 1 – measured H_2 requirement[1]				
Base fuel	2200	22.7	2.18	
Hydrotreatment 1	98	19.6	1.22	0.73
Hydrotreatment 2	9	19.7	0.98	0.83
Study 2 – estimated H_2 requirement from Prelim 1.3 refinery model[2]				
Base fuel	200	15.7	0.73	
Hydrotreatment 1	26	15.6	<0.1	0.94
Hydrotreatment 2	35	7.1	<0.1	6.9
Study 3 – estimated by inhouse model[3]				
Naphthalene removal				2.5

[1] [29], [2] [11], [3] [24]

The hydrogen requirement to remove naphthalenes (to below <0.1%) seems consistent at around 1 – 2.5 kgH_2/tonne of fuel produced. The hydrogen requirement to reach a total aromatic level of 7% is significantly higher at around 6.9 kgH_2/tonne of fuel produced. No data was identified for the hydrogen requirements to achieve lower total aromatic levels; however it is likely to be significantly higher still.

3.5. Techno-economic analysis

A hydrocracker unit might cost £1-2 billion depending on the size while a kerosene hydrotreater (Kero HT) unit is normally 1/3-1/2 of that cost.

The major requirement for the operation of such plant is a source of hydrogen. Currently, <5% of the global production of hydrogen (green) production comes from water electrolysis and about 2/3 comes from Steam Methane Reforming (SMR, grey hydrogen) [33]. During SMR, hydrogen is reacted with steam at 800-900°C and 20-30 bar with the overall reaction of:

$$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2 \tag{3.1}$$

In addition to carbon dioxide being emitted during the reaction, if combustion is to be used as the heat source for SMR, carbon dioxide is also released during combustion of methane (or other fossil fuel) to achieve reaction temperature and might also be emitted during electricity generation for compressors and other utilities. This has a negative impact on refinery emissions profile and is somewhat counter to the LCAF concept.

SMR technology is currently one of the most energy and emissions intensive refinery processes and constitutes around 60% of hydrocracking environmental impact. The requirement for hydrogen for hydrotreating is less, and consequently the impact of SMR on the GHG emissions of the process is lower. This is clearly illustrated in Figure 3.11 by the cyan coloured sections of the histogram.

The development of large scale water electrolysis plant may reduce the need to rely on SMR technologies and lower the GHG impact of hydrogen production, but this process only becomes GHG neutral hydrogen (not involving carbon emissions in production) when renewable electricity is used to provide the energy required.

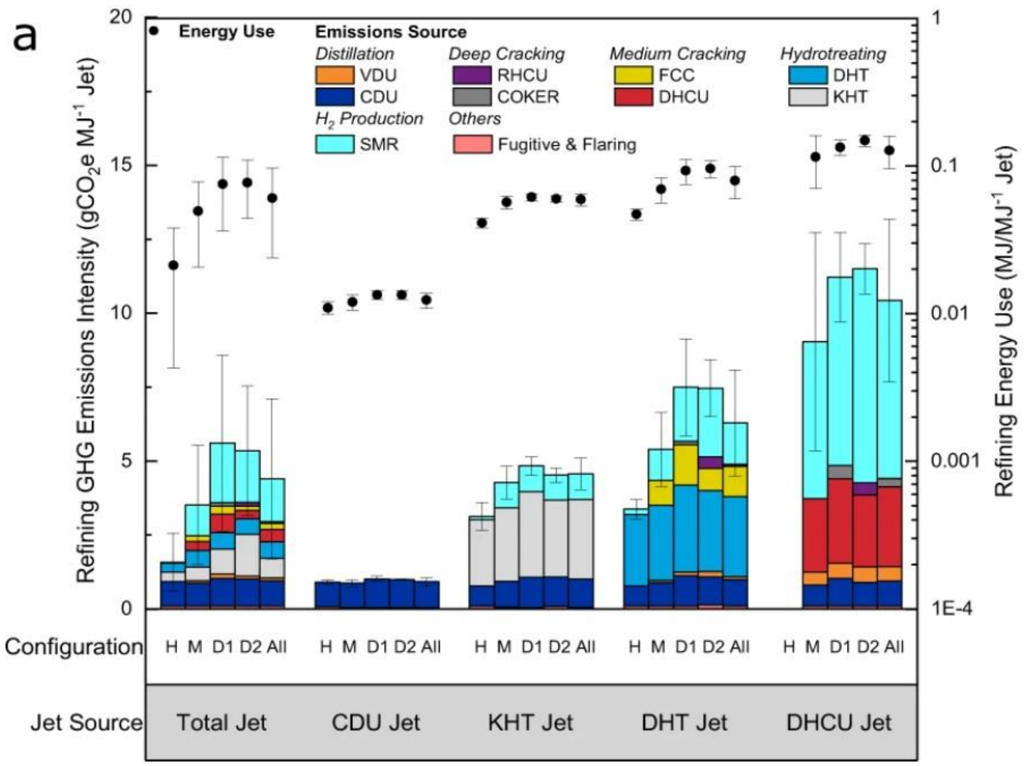


Figure 3.11: GHG emissions and Energy use in the refining of fuel (excluding extraction, transport, and combustion of final fuel) from available refinery technologies [23] note the log scale on the Energy Use axis

Table 3.4 illustrates the main parameters for blue hydrogen from SMR for a suggested 500 t/d hydrogen plant [34]. Suggested build cost is around £250-500m which is roughly aligned with other announced commercial plants [35]. With respect to removal of aromatics using hydrocracking (HC) or hydrotreatment (HT) it will be important to consider the emissions related to producing the hydrogen. The data in Table 3.5 shows about 8 kg CO_2 per kilo of hydrogen. However, this could be reduced to about 4 kg CO_2 per kilo of hydrogen if an adaptation to the standard process known as autothermal reforming was used [36]. Autothermal reforming uses a partial oxidation within the reactor to avoid external heat needed as used with standard SMR removing the need for two CO_2 capture units.

This is roughly in line with modelling studies of the removal of naphthalenes from Jet A/A-1 which reports an LCA increase of around +3.35 gCO_2e/MJ and an increase in fuel cost of around +4.7 USc/L [24]. This study also identified that hydrotreatment costs are more sensitive to upfront capital investment.

Green hydrogen might also be considered in the future, provided electricity cost becomes affordable (about 50 MWh/ton hydrogen), grid connections issues are solved (up to 15 years wait), water bottlenecks and related issues are solved [37].

Table 3.5: Illustration of main parameters for blue hydrogen from SMR [34]

Parameter	Unit	Value
Hydrogen production	kg H_2/h (t/d)	20,830 (t/d)
NG consumption	kg NG/kg H_2	3.16
NG price	\$/GJ	3.7
Water consumption	kg H_2O/kg H_2	9.74
Specific CO_2 emissions	kg CO_2/kg H_2	8.74
CAPEX	\$/kg H_2	0.15
OPEX	\$/kg H_2	0.81
Hydrogen production cost	\$/kg H_2	0.96

Aromatics in jet fuels are complex and may vary depending on the crude refined. Any changes to refining operations for reduction/elimination must be carefully considered as reduction in aromatics may lead to other performance issues, including density, freeze point and other properties. However, changes in available crudes globally, changes in environmental legislation and increasing SAF mandates might offer opportunities for refineries to strengthen their position as low carbon fuel providers, especially by the incorporation of low-carbon hydrogen.

3.6. Overview of bulk components of aviation fuel

The bulk composition of fuel can be broken down into the classes of hydrocarbon compounds fuel molecules introduced in Chapter 2. As stated earlier, conventional fossil fuels are made up of a complex mixture of hydrocarbon species and a small number of trace components which can have beneficial or detrimental effects on the combustion, operability and handling performance. Experimental data on the carbon, hydrogen, sulphur, oxygen and nitrogen containing components in a fuel allow the hydrogen / carbon ratio to be calculated [38].

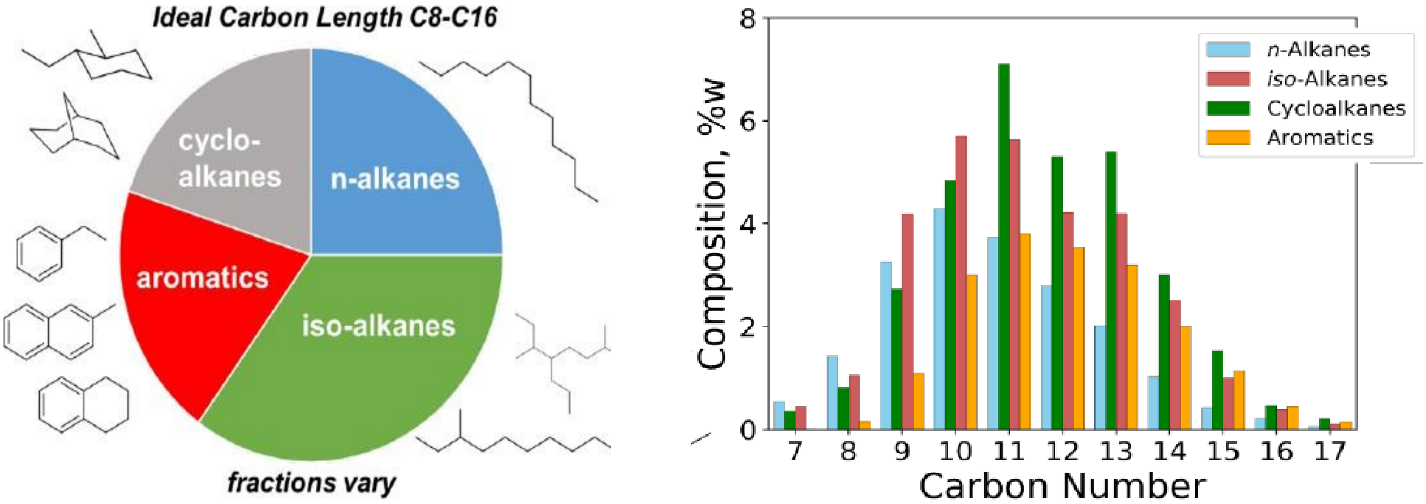


Figure 3.12: Typical aviation fuel composition by molecular class and carbon number [3]

Of conventional fuels in service today, the aromatic concentration remains relatively consistent, (typical between 15% and 20% by volume but can range from 5% to 25% by volume) as the density of the fuel changes between the limits of the specification. Much larger changes are evident in proportion to the iso-paraffinic and cyclo-paraffinic structures present in the fuel.

The carbon (C) and hydrogen (H) content of a fuel can be estimated by the combined use of different analytical and spectroscopic methods such as gas chromatography (GC), mass spectroscopy (MS), H-NMR or C-NMR spectroscopy. Therefore the average HD can be calculated as the weighted sum of mass fractions estimated from 2DGC data for specific fuels in line with the methods introduced in Chapter 2 as follows:

$$HD_{average} = \sum_{i=1}^{n} HD_i y_i \tag{3.2}$$

Where y_i is the mass fraction of a specific molecule as identified in 2DGC and HD_i is the hydrogen deficiency of that specific molecular structure and n is the number of identifiable molecular classes (as detailed in Table 2.1).

Richter et al. (2021) [39] report a HD for Jet A-1 to be around 1.25, depending on the precise fuel chemistry This is close to the lower limit of HD values calculated from the CRC world fuels survey and presented in Figure 3.13 below, which suggests an average for Jet A-1 fuels of around 1.57.

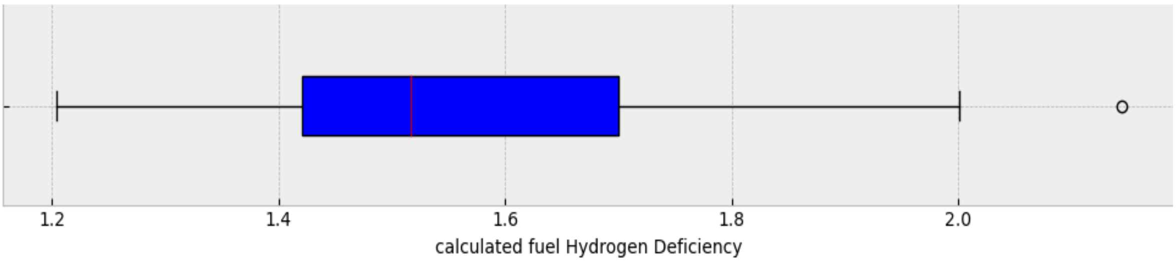


Figure 3.13: Calculated average Jet A/A-1 hydrogen deficiency values from CRC world fuels survey 2DGC data [40]

Whilst an average HD for a fuel is an indication of the average level of unsaturation of a fuel, it does not fully capture the effect of increased levels of hydrotreatment of the fuel chemistries, and subsequent fuel chemistry. Only three datasets have been identified in the literature which explored this impact: Tucker et al. [29], The JETSCREEN project [11] and Kittel et al. [28]. The results of increased hydrotreatment are shown in Figure 3.14 from data provided by the JETSCREEN project.

In common with other studies [28], [29], Figure B.1 (presented in Appendix B) shows clearly the effect of increasingly severe hydrotreatment, firstly removing the di-aromatic (Naphthalene) components and converting them primarily to cycloparaffins and iso-paraffins, which show the largest rise in mass fraction.

3.7. Jet fuel in context of other refinery product streams

Jet A/A-1 aviation fuel is produced and sold as a commodity on a global market. It is processed from crude oil by refiners. The exact composition of the produced fuel is dependent on the crude oil feedstock available to the refiner. Jet A/A-1 is produced as one of a slate of products processed by a refinery, in particular gasoline (petrol) and diesel, both of which overlap the Jet A/A-1 composition. Depending on the refinery configuration the increased use of hydrotreating could impact on these other products as well in both positive or negative ways. A refiner has some ability to alter the final product mix to maximise profitability from the available feedstock and the prevailing market conditions. The main processes available to a refiner include (in increasing energy intensity) straight run, caustic washing, hydrotreating and hydrocracking. Traditionally gasoline and diesel offer a higher financial return to the refiner than Jet A/A-1 and are often prioritised in the production.

Both gasoline and diesel also have specifications which fuel is produced to. These specifications have been used as a tool to reduce the impact of the combustion of these fuels, the most significant for this study is the change in sulphur content in diesel to European Committee for Standardization CEN EN 590 as shown in table 3.6. The first sulphur content diesel specification was established as voluntary in 1994 and replaced with a mandatory environmental regulation in 1998 (Directive 98/70/EC) along with a timeline for achieving fuel sulphur level reductions in 1999 (Directive 1999/32/EC).

Table 3.6: Change in CEN EN 590 European Diesel specification (with a particular focus on Sulphur)

Year	EU Directive	CEN standard	Sulphur content to ASTM D3120* (ppm)	Cetane number to ASTM D613**
1993		EN 590:1993	<2000	49
1996	Euro 2 93/12/EEC		<500	
1999	Euro 3 93/12/EEC	EN 590:1999	<350	51
2004	Euro 4 98/70/EC	EN 590:2004	<50 (“sulphur free” <10 ppm sulphur diesel fuel must be available)	
2009	Euro 5 2003/17/EC	EN 590:2009	<10	

* or IP33, ISO 8754, IP373

** or BS5580, ISO5165

Achieving these lower sulphur specifications required a change in the refining hardware and a significant investment into hydrotreating capabilities in the European Union (where EN 590 specifications apply). As a consequence of these changes to European EN 590 diesels, and the hydrotreating of middle distillate products, the measured aromatic and naphthalene content of Jet A/A-1 dropped over this period, even though the specification limit is 25% and 3% respectively. The measured sulphur content in Jet A/A-1 is also reported in Figure 3.14 as a slightly increasing level of average of 50 ppm, even though the specification limit for sulphur has remained at <3000 ppm.

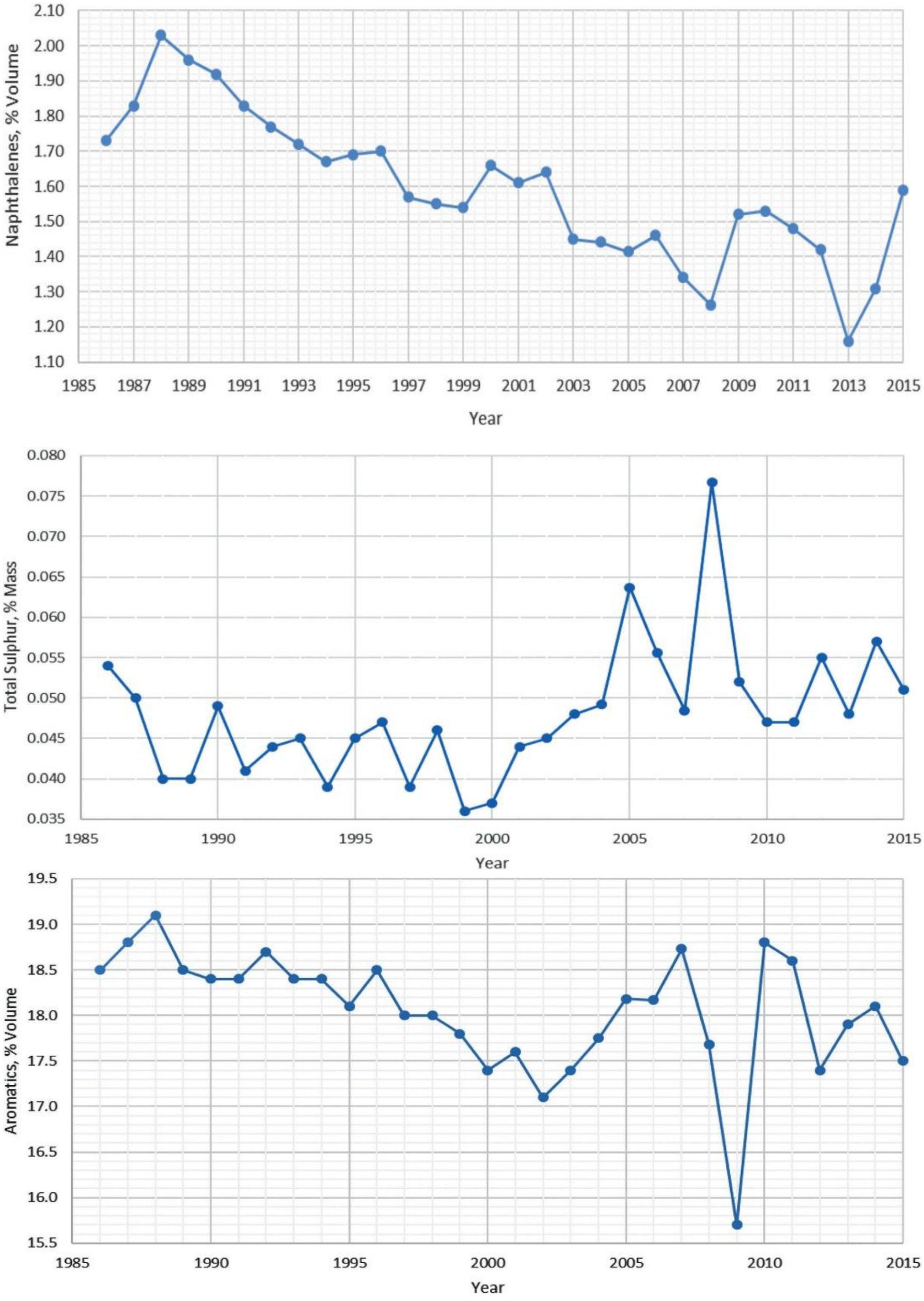


Figure 3.14: 20 year trend in aromatic, naphthalene and total sulphur content in UK Jet A/A-1 [41]

3.8. Speciating the aromatic components of aviation fuel

Taking into account the limitations of analytical methods for identifying specific molecules, we do not have a full picture of the entire chemistry of the fuel. In the fuel specification, the aromatic content of fuel is limited to less than 25% by volume using test method ASTM D1319. As discussed in Chapter 2, This method groups together all aromatics as one.

Further data on composition is available from analysis beyond the fuel specification using 2DGC methods to speciate the aromatic content of fuel. This can provide a more detailed analysis of typical aromatic containing molecules and is shown in Figure 3.15. as a function of the molecular type identified in the 2DGC analysis (a detailed description of the method and its shortfalls is covered in Chapter 2).

Clearly shown in Figure 3.15 is the increasing molecular size and complexity from left (benzene, the simplest aromatic to di-aromatics and benzenes with long alkane tails of C16+). Typically, the concentration of these species in the final product is a function of the composition of the feedstock crude, and the level of hydrotreatment. Increased hydrotreatment (pressure and time at temperature) will result in these more complex molecules being broken down into simpler hydrocarbon structures, preferentially removing the tri- and di-aromatic components.

The contribution that each of these components make to the overall performance or properties of fuel is known to be different and complex, in so much as we are able to characterise the individual contribution of components to the overall system behaviour. The most well-known assessment of the integrated contribution is in the smoke point measurement in the fuel specification. ASTM D1322 Smoke point is a measure of the propensity of any candidate fuel to produce smoke in a simple wick burning lamp. The distance from the tip of the flame and the start of smoke production above the flame is measured (in mm) and reported. If the smoke point is less than 25mm, then it is required to make a separate assessment of the Naphthalene (di- and tri- aromatic) content of the fuel. Clearly, the specification recognises that not all aromatic components in the fuel produce the same impact on performance as measured by the specification. The continued use of this empirical test method shows that fuel composition and contribution of the many individual components cannot be used as a predictor of smoke propensity as it is too complex to analyse and/or calculate in sufficient detail. General trends in smoke production from the broad classes of compounds are known but predicting smoke solely based on these broad classes is not possible.

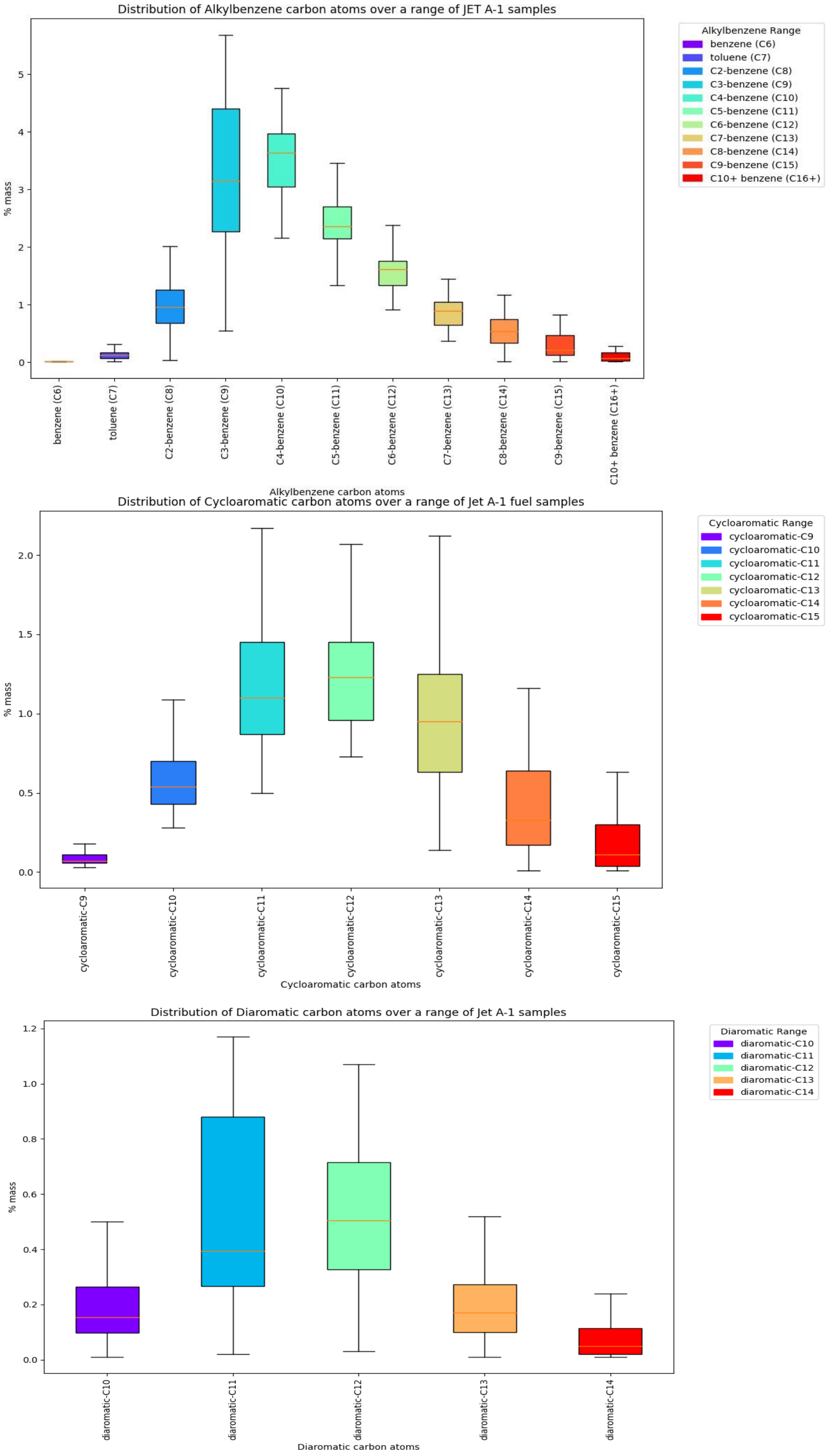


Figure 3.15: Speciation of Aromatic components in aviation fuels from CRC world fuel survey (2007) (adapted from [40])

One of the clear focuses of this study will be to identify research which provides further evidence supporting the argument that the contribution of individual species grouped together as “aromatics” is necessary and may provide a more targeted response than treating aromatics as one class of molecules in aviation fuel.

3.9. Importance of hydrogen content

Several metrics for the measurement of the hydrogen content of fuel have been presented in Chapter 2 including %H content (which can be measured using NMR spectrometry ASTM D3701), HD and H/C ratio.

These metrics can provide some useful guidance as to the likely composition of a fuel. However, in a fuel made up of a complex mixture of compounds, it is challenging to reduce this complexity down to a single number, and it would be misleading to do so. This can clearly be seen in Figure 3.16 which compares a large number of fuel sample D3701 hydrogen contents to D1319 aromatic content. Smaller datasets give an impression of an inverse linear relationship between aromatic and hydrogen content – which is broadly true but a wide range of %H can be produced for a given aromatic content, say for example the range in %H at 25% aromatics. This is because the other components in the fuel, such as cycloalkanes, di-aromatics and heteroatomic species as indicated in Figure 2.1, also contribute to the hydrogen content of a fuel to varying degrees as suggested in Table 2.1.

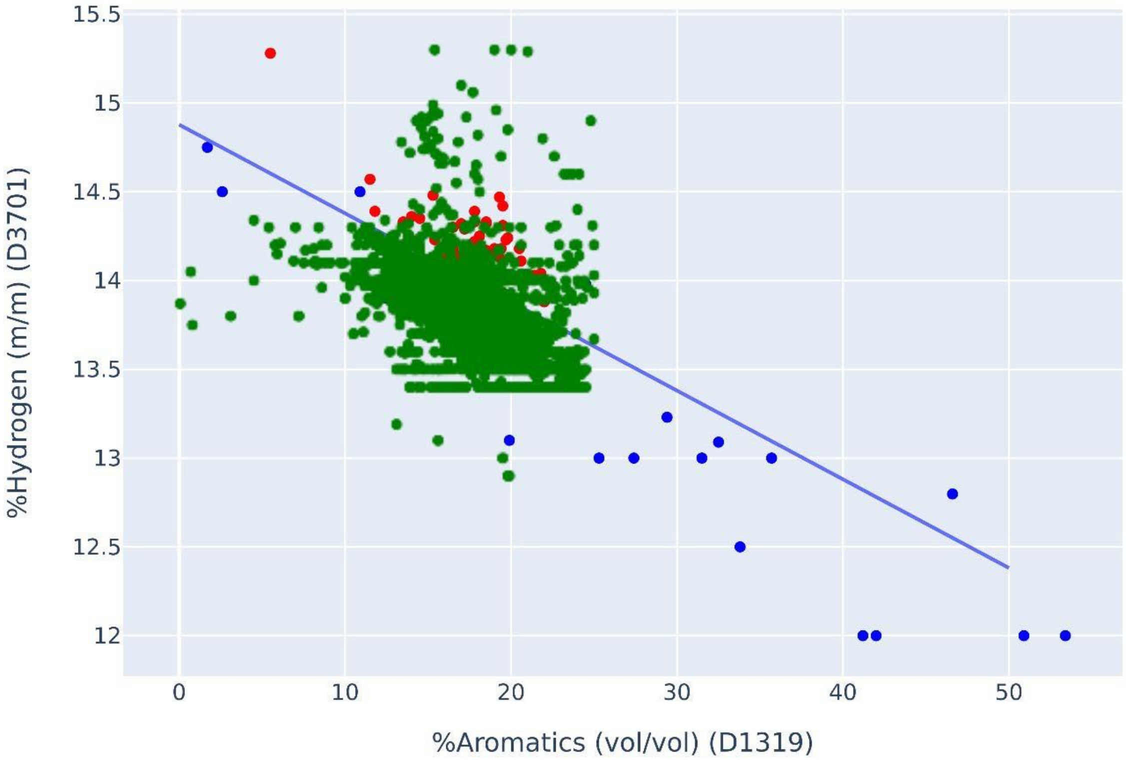


Figure 3.16: Correlation between ASTM D1319 %Aromatics and D3701 %Hydrogen content from a range of fuels studies and surveys (blue line – proposed linear correlation [42] blue data – 1980s studies [43] red data - CRC world fuels survey [41], green data – PQIS fuels survey [44]

In general, a high H/C ratio (high %H, low HD) tends towards a high energy content per unit mass. Low H/C ratio fuels (low %H high HD) tend to have lower thermal stability (Chapter 4) and produce higher levels of smoke and soot (Chapter 5) [45]. This is particularly undesirable for gas turbines internally as the soot particles deposit on the turbine blades and dramatically increase corrosion [38] and increase thermal loading by increased flame radiation.

In many emissions studies, the hydrogen content (%H) is reported as the key variable against which results are plotted. It is important to understand that this may mask the effect of specific molecular structures in the fuel as molecules of identical hydrogen content can have vastly different properties of importance for aviation. This is well captured in the analysis presented in Figure 3.17 [46], showing the range of calorific values possible for different hydrocarbon structures of the same carbon content. This is further reinforced by the fact that NMR based hydrogen measurement methods are relatively simple and easy to use but have been rejected by the industry as not a useful specification test method to control combustion properties.

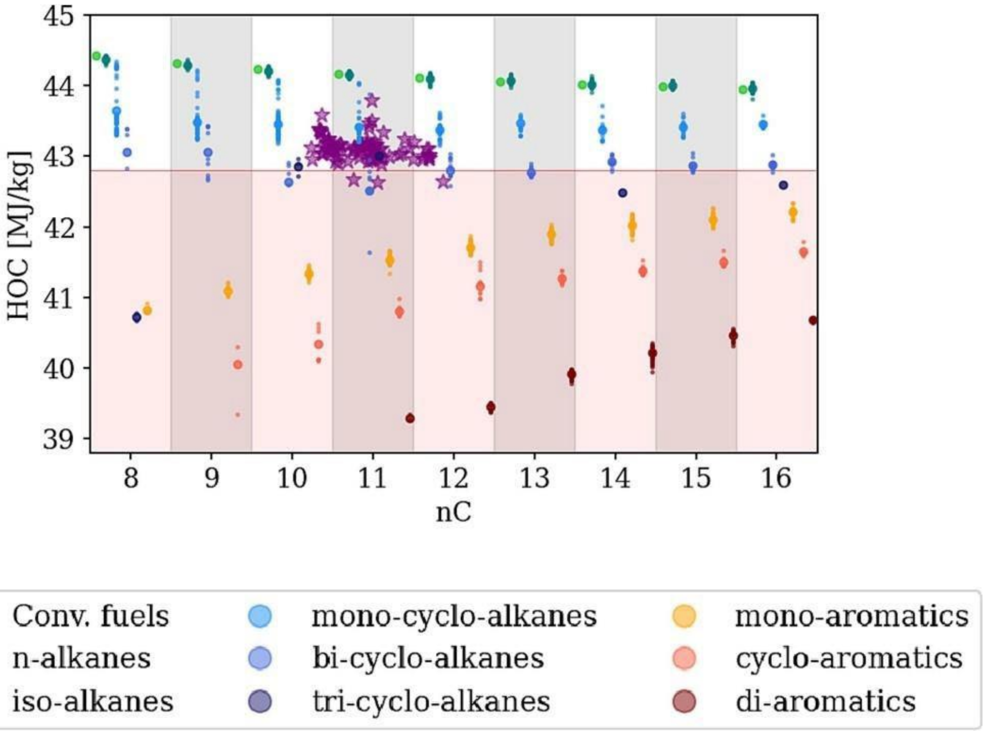


Figure 3.17: Variation in energy density per unit mass for fuel carbon numbers and molecular structure, red line represents the limit of the fuel specification [46]

3.10. Density and calorific value

Discussions on the impact of aromatics on fuel performance often starts with their impact on the density and energy density of fuel. The more compact, carbon rich molecules of the aromatic form have higher density than straight (normal-) or branched (iso-) alkane structures. This higher density is primarily due to the hydrogen to carbon ratio of the aromatic molecule which consequently results in a lower energy density per unit mass, as is discussed in Chapter 2. In terms of the impact on the performance of aircraft, low aromatic, high energy density by mass and by volume are desirable, however typically higher energy density by mass fuels have lower densities (higher hydrogen content and lower carbon content) – theoretically there can be up to a 3% reduction in CO_2 emissions in flight, due to the lowest possible carbon content hydrocarbons and they require a lower mass flow rate of fuel due to the higher energy density per unit mass both theoretically [47] and in flight tests such as the Air New Zealand (ANZ) flights at 50:50 blend ratios [48]. Conversely the volumetric flow rate increases due to the lower density of the fuel which can impact on pump performance.

In addition, the decreased volumetric energy density (MJ/L) will require a larger volume of fuel to be transferred through the engine and airframe pumping system for a comparable chemical power to be delivered to the engine combustor. This is of concern for high pressure pumps in the fuel system which are volumetric displacement devices (gear pumps and piston pumps in which a fixed volume of fuel is drawn into the device, pressurised and discharged at a higher pressure) and will be required to operate at a higher speed to deliver the same energy.

The overall chemical composition determines the density of hydrocarbon fuel. In general, the density of hydrocarbon fuels decreases in order: aromatics>cyclo-paraffins>paraffins for hydrocarbons with the same number of carbon atoms. This indicates that the hydrocarbon fuels with a lower H/C molar ratio have a higher density (with the same carbon number).

The density of aviation fuel can be enhanced by increasing the cyclo-paraffin content. Additionally, the density of the hydrocarbon blend, consisting of n-, iso-, and cyclo-paraffins, demonstrates linear growth with an increase in cyclo-paraffin content. Cyclo-paraffins with cis configuration typically possess a higher density than their trans configurations (symmetry structure) due to the twisted structure of cis configuration, e.g., cis-decalin (0.897 g/cm3) versus trans-decalin (0.870 g/cm3).

The number of total carbon atoms will also influence the fuel density. The increase in the total carbon number of most hydrocarbons, except alkylbenzene and naphthalene, leads to a high density. The density of alkylbenzene remains almost constant, whereas that of naphthalene declines with the increase in carbon number.

Energy density per unit mass, is the energy released from the complete combustion of fuel, with resulting products in the gaseous state. It serves as an important indicator of the energy content of aviation fuels, directly influencing factors such as range and payload capacity. Moreover, energy density per unit mass plays a central role in determining combustion characteristics, such as stability, efficiency, and emissions of aviation fuels.

The energy density per unit mass of Jet A-1 must be greater than 42.8 MJ/kg for conventional fuels and/or fuel blends in order to meet DEFSTAN 91-091. Figure 3.19 presents the distribution of net heat of combustion across a large number of Jet A-1 samples.

In general, the gravimetric net heat of combustion of different types of hydrocarbons decreases in the following order (with the same carbon number): paraffins>cyclo-paraffins>aromatics.

The energy density per unit mass of n-paraffins and iso-paraffins decreases with the increase in the carbon number as a result of the reduced H/C molar ratio. However, for the cyclo-paraffins increase in the total carbon numbers results in no changes in the energy density per unit mass. However, for alkylbenzenes this results in an increase in energy density per unit mass. This is attributed to the H/C molar ratio of cyclo-paraffins which remains constant, whereas that of the aromatics increases with the rise in carbon atom number. Single ring alkylbenzenes have much lower energy density per unit mass. However, the higher the total number of carbon atoms, the more energy is available, until a plateau is reached, starting from C10, as shown in Figure 3.19

The change in energy density per unit mass may also result in a reduction in the fuel air ratio (FAR) in the combustor which will shift the location of the flame in the combustor. This will be discussed further in Chapter 5.

3.11. Cetane number

The Cetane number (ASTM D613) of a fuel is an indicator of the speed of combustion and compression required for auto ignition to take place. Higher cetane numbers suggest a more rapidly combusting fuel and a reduced ignition delay time. Typical cetane numbers for jet fuel range between 49 and 51. As the HD of the fuel decreases (as more hydrogen is added to the molecule and it becomes saturated), the cetane number will increase, reducing the ignition delay time.

Cetane numbers are not part of the specification for Jet A/A-1. They have been shown to be critically important for the use of fuel in piston engines and are correlated to the lean blow out performance of aviation fuels (to be addressed in Chapter 5).

3.12. Discussion

Although limited data are available for specific crudes, the data that is available suggests increasingly severe hydrotreatment will convert the fuel components with the highest HD first – this means di- and tri- ring aromatics content before mono-aromatic content. In parallel the hydrotreating process also removes the sulphur and heteroatomic content from the fuels. Indeed, this is the reason why most of the hydroprocessing capacity in Europe is present, to reduce the level of Sulphur in Diesel fuels. To illustrate this process simply, the impact of hydrotreatment of the fuel physical properties can be seen in Figure 3.18. This will be added to in subsequent chapters. A limited number of studies have explored the impact of increasing hydrotreating capacity to remove (in order of energy cost): sulphur, naphthalene and mono-aromatics.

The increase in energy required to remove successively lower HD components from the fuel is not linear although the exact relationship needs to be established in the literature. In the most extreme cases, severely hydrotreated products with low or zero aromatic content will start to resemble the chemistry of neat SPK products specified as part of ASTM D7566 Annexes. Drawing wider conclusions on the production energy requirement from this comparison is potentially flawed however as the crude / synthetic crude feedstock may not have the same composition, particularly when considering the aromatic components of the crude.

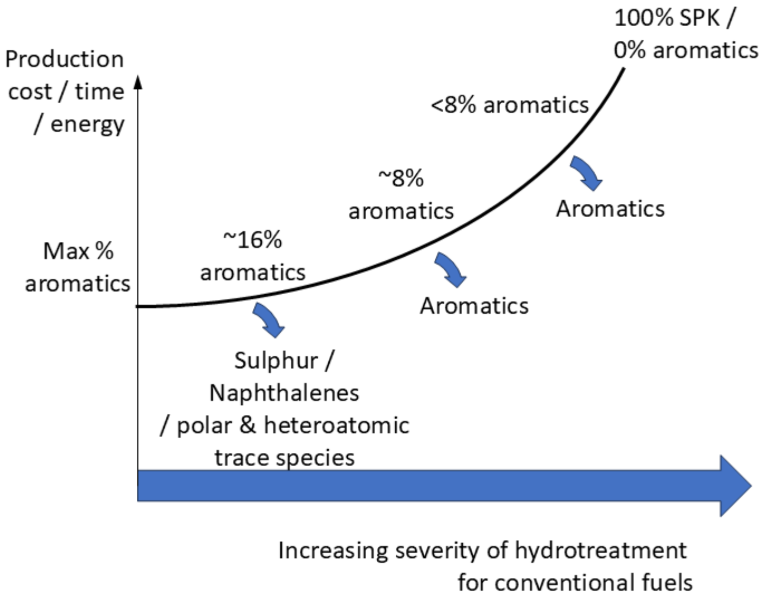


Figure 3.18: Impact of increasing severity of hydrotreatment on fuel chemistry

The volume and type of aromatic compounds in aviation jet fuel exhibits large regional variations depending on the: (i) source of the original crude oil; and (ii) refinery process; and (iii) type of jet fuel. To ensure consistency in jet fuel composition and safe operations, current aviation jet fuel standards mandate the aromatic content to be within a specified range of min. 8% (ASTM D7566) and max. 25% (ASTM D1655) by volume. The minimum aromatic content of 8% serves as a safety consideration by promoting the swelling of elastomeric seals, thereby preventing leakages in the aircraft fuel system [49].[50]; while the upper limit of 25% is required to ensure that the fuel's lower calorific value (LCV), or energy content per unit mass i.e., the thermal energy produced by combusting a unit mass of fuel, exceeds the predefined threshold of 42.8 MJ kg^{-1} and ensures that the smoke and particulate matter emission production is limited to an acceptable limit (ASTM D1655) [51] and other related properties are within required limits. Data from different experimental campaigns suggest that conventional kerosene fuels have an aromatic content that generally ranges between 15–22%. Notably, sustainable aviation fuels (SAF) which are produced via the hydrotreatment process, such as those from Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK) and the hydroprocessed esters and fatty acid SPK (HEFA-SPK) pathways, do not generally contain any aromatic compounds [52] [53]; [54]. To comply with the minimum aromatic content (8%), these fuels can either be blended with conventional fuel up to a 50% blending ratio by volume (ASTM D7566-21) or augmented with synthesised aromatic kerosene (SAK). Reducing the aromatic content of conventional fuels may challenge this blending ability.

In addition to the difference in organic compounds, aviation jet fuel also contains naturally occurring sulphur compounds with concentrations varying depending on the origin of the crude oil and refinery technology (see earlier). According to global fuel supply data, aviation jet fuel typically has a fuel sulphur content (FSC) that ranges between 400 and 800 parts per million by mass (ppm) [55], [41]. Around 25% of the global finished jet fuel supply has an FSC below 300 ppm, while 5% of it exceeds 2000 ppm [55]. The positive association between the FSC and the deterioration of air quality and human health [52], [53], [56], [57] serves as a key motivating factor for aviation jet fuel specifications to establish a maximum limit for aviation FSC which is currently set at 3000 ppm (ASTM D1655). Conversely, sulphate particles, formed from the SO_2 emitted at altitude, results in a negative radiative forcing from the aerosol radiation interaction effect and potentially a much larger negative forcing from the aerosol cloud interaction effect [58], which is explained in Chapter 7. While most aviation jet fuels have FSC levels significantly below this regulatory limit (< 3000 ppm), and despite the global trend of reducing the FSC in ground-based transportation, there are currently no plans in the near- and medium-term to revise the regulatory limits for FSC in aviation jet fuel specifications.

Data compiled from previous experimental campaigns have shown that the volume of aromatic compounds changes several fuel properties (Table C.2 in Appendix C), including the hydrogen content, LCV, and density. Firstly, there is a negative linear relationship between the volume of fuel aromatics versus the hydrogen mass content, and the hydrogen mass content is positively correlated with the water vapour emissions index (EI H_2O) [59]. Consequently, the energy density by mass of aromatic compounds (41 – 42.5 MJ kg^{-1}) are, on average, 4% lower than that of aliphatic compounds (42.5 – 44.5 MJ kg^{-1}) [60]. For these reasons, an increase in the fuel aromatic content generally lowers the fuel's overall H/C ratio, which, in turn, reduces the fuel energy density by mass and will lead to a higher relative CO_2 emissions index of a maximum of -3% for a fuel with no aromatic component in comparison to conventional fuel. Thirdly, the volume of fuel aromatics also exhibits a positive linear relationship with the fuel density, and a higher fuel density can impact the fuel atomisation process, leading to larger fuel droplet sizes, incomplete combustion, and the resulting emissions [61] as will be discussed in Chapter 5. This may also result in increased contrail formation; however a number of other non-CO_2 factors needs to be taken into consideration such as the change in soot mass and number and their connection to ice crystal number. This will be addressed in Chapter 6.

3.13. Research gaps

Further work is required to assess the implications of decarbonising the production of aviation fuel in particular nation states whilst considering the imbalances created by reducing crude oil consumption at different rates in different countries.

More severely hydrotreating conventional fuels will start to reduce the total aromatic content of Jet A/A-1. This may have consequences for the ability to blend conventional fuel with SAF as the 8% aromatic limit will be reached at increasingly lower blend ratios. Another route to increasing the sustainability of producing aviation fuel may be to co-process synthetic crudes with conventional crude streams at the refinery. This is currently limited to a 5% blend (HEFA/FT crudes) [9]. The aromatic composition of these crudes is not as well investigated and may mean that the average aromatic content of such co-processed products is different from that of conventionally refined fuel.

Finally, the selection of where to use hydrogen to have the most overall GHG emission reduction is not a simple exercise and requires further understanding.

3.14. Conclusions

Aromatics in jet fuels are complex and may vary depending on the crude, refinery technology and product slate of the refinery. Any changes to refining operations for reduction/elimination must be carefully considered as reduction in aromatics may lead to adverse issues, including density, freeze point and other properties. However, changes in available crudes globally, changes in environmental legislation and increasing SAF mandates might offer opportunities for refineries to strengthen their position as low carbon fuel providers, especially by the incorporation of green hydrogen and LCAF strategies. However, the increased use or severity of hydrotreatment to reduce aromatics will inevitably impact refinery energy balance and environmental performance that has to be balanced against the potential benefits of low aromatic jet fuels. [Note, confidence statements below are preliminary and are subject to further discussion and feedback]

1. Increasing the level of hydrotreating to remove aromatics will incur significant energy and financial costs in the production of Jet A/A-1. Preliminary studies suggest that the impact of removing naphthalenes alone would be +4.7 USc/L and +3.35 gCO_2e/MJ. **(high confidence)**

2. The impact of such changes on refineries has not sufficiently been assessed in the literature, and further studies are required to establish the likely impact of changes in the level of hydrotreating required. **(high confidence)**

3. Reducing aromatics in fuel will limit the blending capacity of conventional fuels with SAF. **(high confidence)**

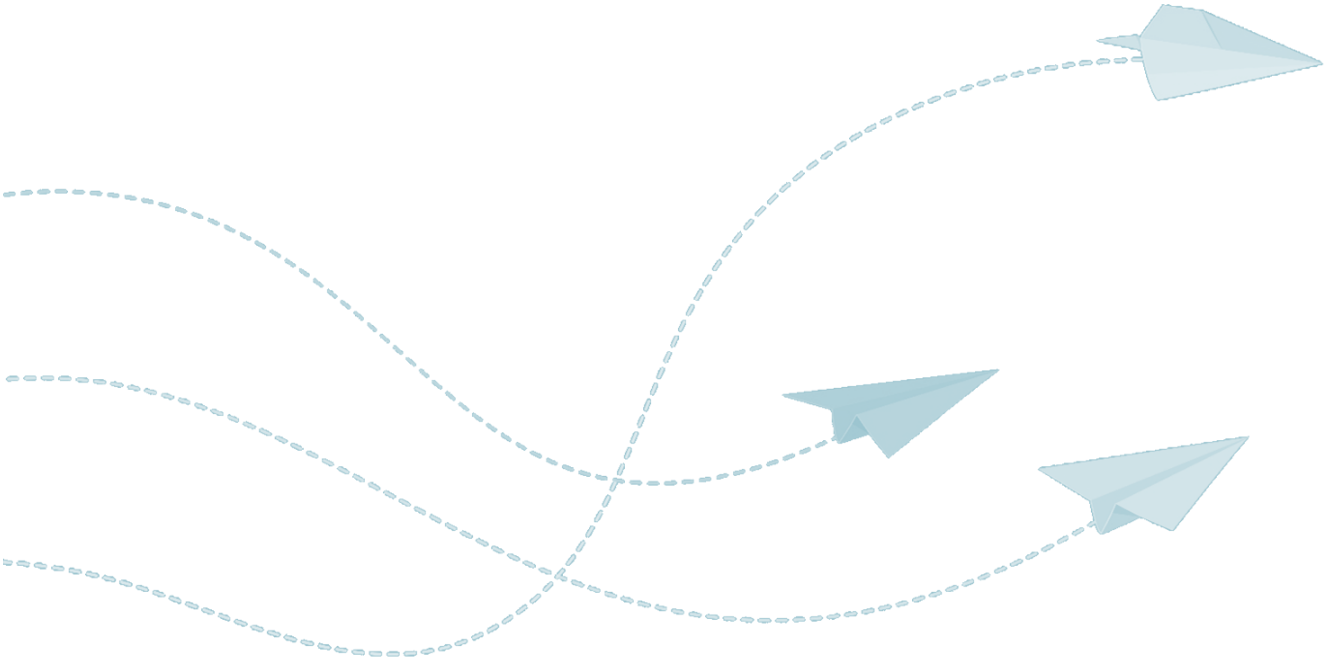
4. Large increases in H_2 production will be required to reduce the aromatic content of Jet A/A-1. **(high confidence)**

5. Lowering the fuel aromatic content increases the fuel energy density by mass by a maximum of 3%, which in turn, lowers the aircraft fuel consumption and CO_2 emissions due to the higher hydrogen content. **(very high confidence)**

6. Higher hydrogen content will increase the water vapour emission. **(very high confidence)**

7. If adopted at a large scale, this will result in a reduction in the density of fuel, and result in higher fuel volume uploads to aircraft to meet the comparable energy level requirements for flight. Simultaneously, the uploaded mass of fuel will be reduced due to the higher energy content per unit mass. **(high confidence)**

8. Hydrotreating to remove aromatics, will also remove heteroatomic and polar trace species from the fuel which can have benefits (thermal stability) and risks (lubricity and storage) this will be addressed in Chapter 4. **(high confidence)**



4. Impact of aromatics on engine and airframe systems

Summary

The presence of aromatic compounds in jet fuel as a natural component, has been taken advantage of in the design of engine and airframe systems. While there is a specified maximum aromatic content of 25% (by volume), there is also a minimum of 8% specified and/or implied under current international fuel standards. This chapter outlines some of the complex interrelationships between fuel properties in terms of physical and chemical properties, and composition, with the engine, airframe and ground-handling facilities. Increased hydrotreatment will likely reduce the lubricity of fuel and the storage stability of the fuel as sulphur containing molecules will be removed because of hydrotreating to remove aromatics. Lubricity and storage stability of fuels can be improved by adding commercial additives to the fuel. However, this increases the cost of fuel, and the risk of mis-dosing in the supply system. One of the functions of aromatics is to ensure adequate swell of certain seals. Elastomeric seals are used throughout the fuel supply system and must maintain their integrity to prevent leakage of fuel. These elastomers have been developed with the assumption that aromatic compounds will cause swell in a predictable, well-quantified linear manner, for the main types of seal used. Were aromatics to be absent or severely reduced in jet fuel, other compounds would need to take over the swelling function, or alternative elastomers that do not depend on fuel components to swell their volume and provide seal integrity. Increased hydrotreatment or hydrocracking of the fuel to reduce aromatics may also have other consequences that need to be carefully considered and quantified, such as the propensity to form deposits, its thermal stability. One of the classification of compounds that could 'substitute' aromatics' role in seal swell are cycloparaffins. Some literature exists on this but is limited and potentially contradictory. It is thought that cycloparaffins would have the desired effect of reducing soot emissions although this has a poor evidence base (lack of). In summary, there are significant research gaps on the specific role of cycloparaffins as a functional substitute for aromatics in engine and airframe systems, and their related impact on combustion and soot emissions.

4.1. Introduction

Since the advent of aviation, hydrocarbon fuels have provided the energy for propulsion on board aircraft and have operated in conjunction with internal combustion engines and a fuel supply system to produce the required thrust for flight. The overall energy efficiency of aircraft and engines has improved with successive design iterations with very few changes in the composition of fuel. The most recent change in fuel chemistry was the transition from aviation gasoline to kerosene which occurred as the gas turbine overtook the piston engine as the prime mover for commercial aviation in the 1950's [62].

Published research into the impact of changes in fuel chemistry on aviation have followed the previous "security of supply" crises in the late 1970's / early 1980's, mid 1990's and the increasing "security of the environment" concerns from the late 1990's onwards [63]. Although the reasoning behind the research has varied, the content and focus of the programmes were very similar and therefore conclusions relating fuel composition to performance are still valid and will be included in this review.

To understand the impact of a low or zero aromatic fuel on the operation and performance of aircraft and fuel systems it is necessary to go beyond the specification tests and discuss the impact on the overall performance in the aircraft and engine under all conditions. Conveniently the ASTM D4054 process can be followed to explore this effect and illustrates the level of complexity and rigour required to assess the impact of reduction of the aromatic component in the fuel or indeed manage any change to the fuel [10]. This chapter will discuss the impact of changes in aromatic content of conventional fuel through the process of hydrotreatment from the perspective of the engine and fuel supply system from refinery to aircraft.

Importantly, the fuel and fuel system (including the engine) operate in partnership with each other and should be regarded as an integrated combined system rather than two separate elements. The consequence of this is that if the fuel characteristics are changed, the combustor and other components of the fuel supply system may need to be redesigned to optimise the power output and to minimise any undesired side effects. Care should be taken in extrapolating the effects of fuel composition on performance without considering the design. The properties of fuels are not independent from each other, and an undue focus on changing one aspect of the fuel will have an impact on other fuel properties. The complexity of the problem is illustrated in Figure 4.1.

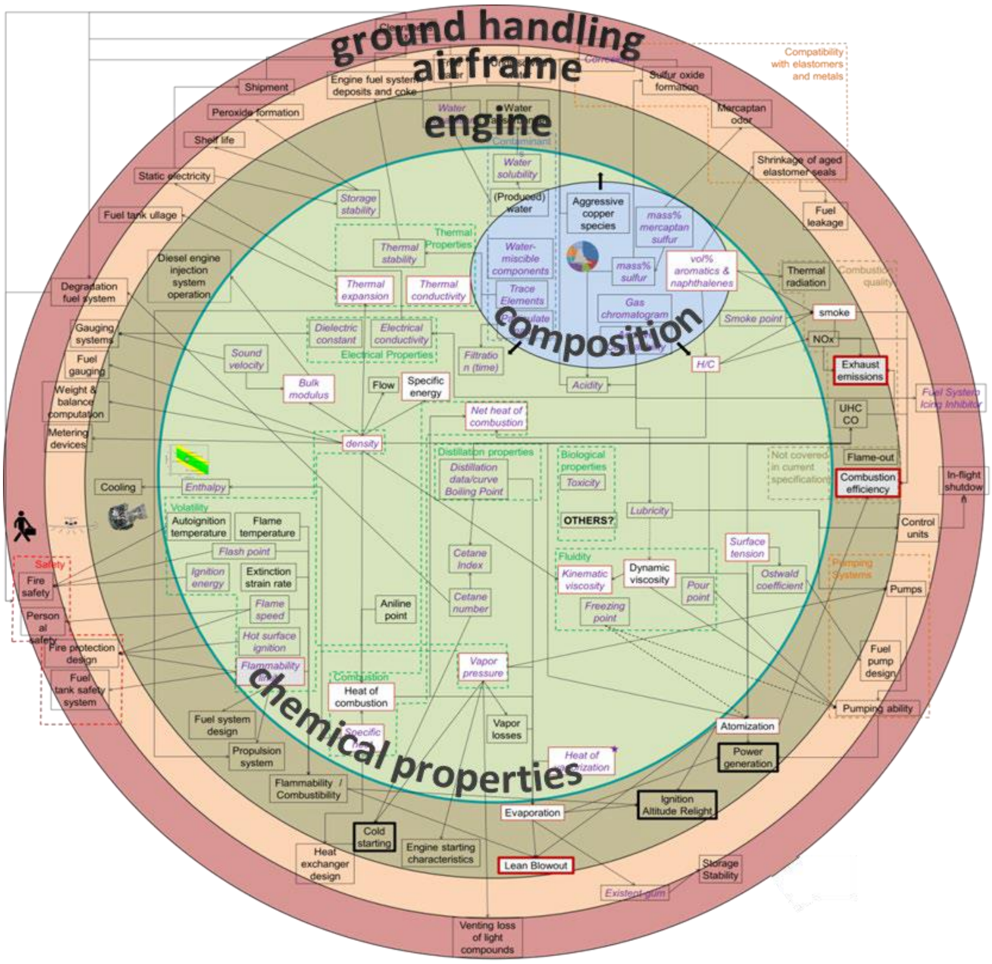


Figure 4.1: Interrelation and connection between fuel properties [12]

It is worth noting that Rolls Royce and Airbus have committed to developing their engine and airframe architectures to be compliant with a 100% SAF, which will have essentially zero aromatic content [64].

The fuel is one of the few systems in aviation that does not have a system backup i.e. it is classed as a single mode failure system, the consequence of this is that problems due to the fuel represent a critical issue for the performance and safety of the aircraft. Other important impacts on gas turbines as an example are shown in Fig 1.2.

Current specification restrictions on the blending of conventional and synthetic fuels require a minimum aromatics level of 8%. This limit is based on operational experience to ensure that the required "fit for purpose" properties are maintained and do not present any negative impact on the performance of the fuel in use [10]. The main concern is compatibility with elastomeric materials, but other issues have to be considered. The more detailed understanding of this limit is an active area of research for the fuels community.

4.2. Lubricity

Aircraft and engine fuel system components rely on fuel to lubricate their rotating and sliding parts [9]. The effectiveness of a fuel to provide lubrication in such equipment is referred to as the fuel's lubricity [65]. Most fuel systems and components experience hydrodynamic lubrication most of the time and no contact between moving surfaces as the fuel provides a liquid barrier. The thickness of the barrier or film is dependent on fuel viscosity and surface to surface movement and loading. At extreme loading surface to surface contact may occur and this changes the boundary lubrication regime. Boundary lubrication regimes are where fuel lubricity plays a critical role. At a fundamental level, lubricity is a combination of the physio-chemical interactions between the fuel and the surface, including van der Waals forces bonding fuel components to the surface providing lubrication, to prevent metal to metal contact at a micro-level or in extreme cases metal to metal transfer. This can be prevented by surface active trace materials in the fuel carried over from processing, but if these are removed by severe hydroprocessing, they have to be replaced with lubricity improving additives [65].

For aviation fuels, the lubricity performance of the fuel is controlled by a tribological wear test known as the Ball on Cylinder (BOCLE) test. The range of BOCLE results for conventional fuels in service is shown in Figure 4.2. In conventional fuel, Although the DEFSTAN 91-091 specification mandates a wear scar diameter of less than 0.85mm, determination of lubricity is only required in ASTM D1655 if the fuel contains more than 95% hydro processed material or at least 20% severely hydro processed material [9]. It is important to recognise that lubricity is an artefact of the test used to measure it and not an absolute property of the fuel. Although it may not be an absolute measurement, fuels which have a BOCLE result of < 0.85mm wear scar diameter do not cause issues in service.

It is important to note that increases in hydrotreatment and/or increased hydrotreatment severity will lead to a reduction in the lubricity performance of the fuel to the point where corrective action will be required to avoid engine component life issues using additives.

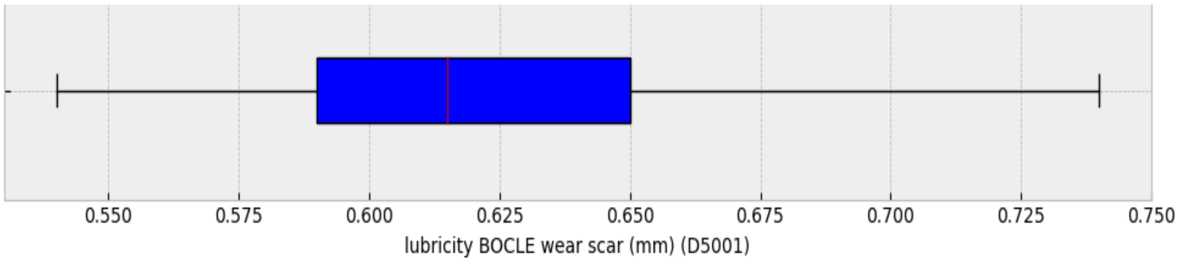


Figure 4.2: Range of conventional fuels lubricity adapted from CRC World Fuels Survey [14]

The lubricity is not solely affected by the aromatic component in the fuel (average 16%) [14] or by the total sulphur in the fuel (average 400 ppm [14]), but a combination of the above and the polar species (ppm and ppb level) removed by increasingly severe hydrotreatment [65]. Several previous in-service investigations into poor lubricity performance have taken place since the mid- 1960s, initially due to the wear and seizure of piston type pumps [66]. A clear link between poor lubricity was established to refinery practices such as hydrotreating and clay treatment used to upgrade the Jet fuel product. There have been a small number of issues in service for pumps and other components in aircraft in somewhat extreme conditions using a single supply source for refuelling, say a single refinery output and is more likely to affect smaller engines used for short haul flight. Sensitivity of hardware to lubricity is more an issue for older hardware designs that still may be in service, so need to be accommodated. Larger, more modern aircraft are more likely to pick up fuel from different locations and average out the quality of the fuel [66] and be less sensitive to lubricity.

Tucker et al. [29] completed a pilot scale investigation into the impact of reducing sulphur content through successive hydrotreatment, clearly showing a drop in the lubricity performance from a wear scar of 0.51mm at a sulphur content of 2200 ppm to 0,79mm at a sulphur content of 9ppm. Perhaps the most relevant large-scale study was carried out in the US Army Forces following the Energy Security Act in 1980 which focused on assessing severely hydrotreated shale oils for producing jet fuel. They identified that the high level of hydrotreatment required resulted in a poor performance of fuel and deemed it necessary to introduce lubricity additives [67].

Current solutions to improve the lubricity of hydrotreated fuels are based around blending with 10-20% of non-hydrotreated conventional fuels [68], [69].

Secondly using additive packages such as corrosion inhibitors / lubricity improvers (specifically Innospec DCI-4A and Nalco 5403 at a maximum dosage of 23 mg/L and minimum dosage of 9 g/cm^3 and 12 g/cm^3 respectively). Although such additives are routinely used in military fuels [9] and may be used in civil aviation, there is considerable reluctance in the industry to the need to mandate corrosion inhibitors / lubricity improving additives for cost and safety reasons. Although the exact composition of these packages is proprietary, it is known that they are polar in nature, these additive packages may be depleted in the fuel by adsorption onto fuel wetted surfaces, and dosing rates need to be carefully assessed. They can have negative effects on fuel filtration and water separation characteristics of the fuel. Therefore, it is recommended to avoid higher dosing of additives wherever possible [9].

4.3. Beyond specification testing

Standard specification testing measures basic properties to ensure the production process is under control but does not measure all critical properties. These are assumed to be within limits if all the specification parameters are met. These assumed properties are referred to as fit for purpose properties (FFP). A wide number of fit for purpose tests are carried out as part of the ASTM D4054 process as part of the management of change for new blends. These measure a wide range of fuel performance parameters required to ensure the fuel behaves with accepted norms under all conditions, which are necessary to demonstrate no negative impact of the fuel on the fuel system and engine performance, operability, emissions, and cost of ownership, and most importantly, airworthiness. These are not regularly tested for conventional fuels, however such a change in reducing the aromatic content of fuel through increased hydrotreatment would require confirmation of no negative effect (unforeseen consequences) through a programme to comply with the management of change requirements in ASTM D4054 [10].

4.4. Fit for purpose tests – seal swell

One of the principal interactions between the aromatic content of fuels is with elastomeric materials used throughout the fuel supply system. These elastomers are present in O-rings, bladders and seals between metallic components in the fuel system and are designed to ensure that there is no leakage of fuel in its path from refinery to combustor.

The three primary seal materials are used throughout the fuel supply system and are detailed in Table 4.1 below.

Table 4.1: Common Elastomer Seal materials

Name	Benefits	Drawbacks
Nitrile	Operates well at low temperatures, most common in ground handling infrastructure. Used widely in aircraft tank systems for their very low temperature capability.	Poor high temperature performance. Strong swell interaction with aromatic content in fuel (i.e. sensitive to fuel composition).
Fluorosilicone	Intermediate temperature performance, most common on modern aircraft in low / medium temperature regions of fuel system.	Less sensitive to aromatic content of fuel – within an acceptable range for volume change.
Fluorocarbon (viton)	High temperature performance, most common in engine fuel system core regions.	Relatively unaffected by aromatic content of fuels. Glass transition temperature around -12°C, so not adequate for aircraft tank applications.

In particular, the nitrile seals used for their low temperature performance in the fuel supply system are sensitive to the aromatic content of the fuel. When the fuel and the elastomer come into contact, the elastomer will appear to swell, and it absorbs a small percentage of the small molecular volume aromatics into spaces between the polymers in the polymer matrix. Ultimately, this is a positive effect for the fuel system as a swollen seal will provide more protection [70].

The strong correlation between aromatic content of fuel and the volumetric change of seals can be seen in Figures 4.3 - 4.4 below, and a clear trend can be seen [71]. However, subsequent work has shown that not all aromatics cause similar levels of swell, and some cause larger levels of swell [72].

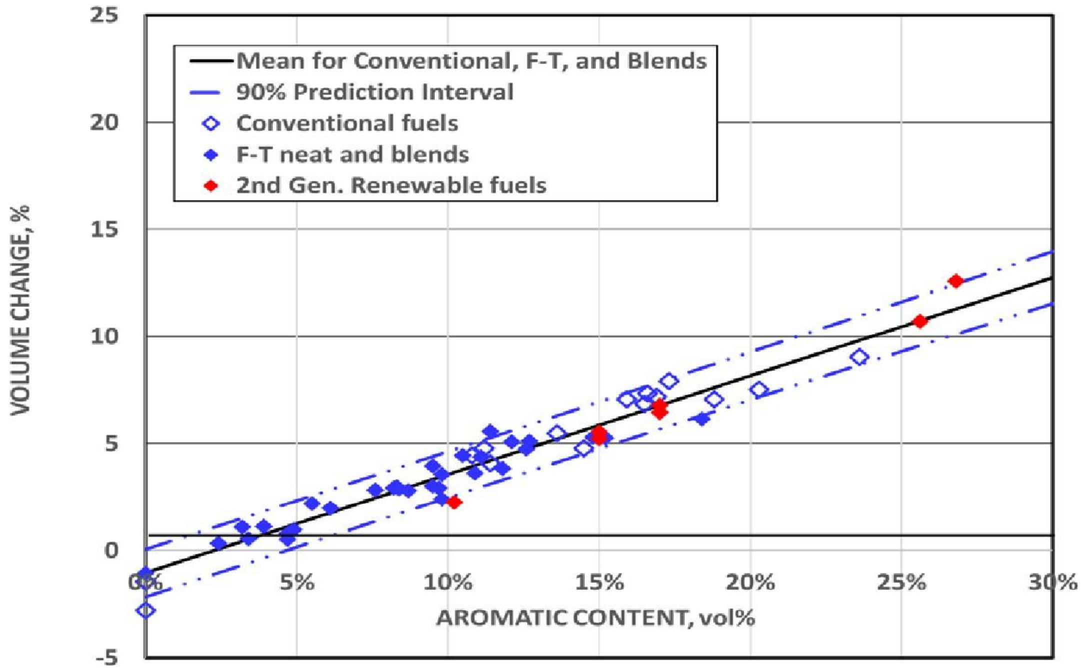


Figure 4.3 – volume change for nitrile seals vs aromatic content [71]

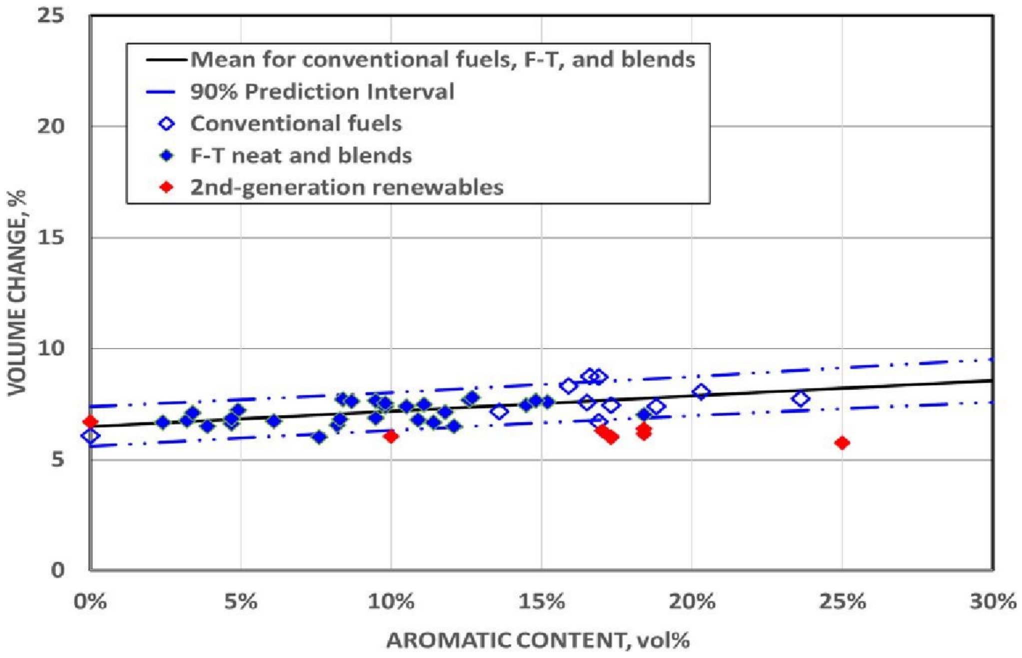


Figure 4.4: Volume change for fluorosilicone seals vs aromatic content [71]

4.5. Fit for purpose tests – thermal stability measurement

Propensity to form deposits

After the fuel has been processed, stored and loaded onto an aircraft, it is used as a heat sink in the engine and a lubricator in a number of engine components, prior to combustion. Fuel is used as an essential coolant for many aircraft and then engine systems and so reaches high temperatures. The fuel is used in this way so that as the fuel enters the combustor that heat is recycled and therefore provides useful heat. This type of fuel-based heat management is essential to improve overall aircraft efficiency.

The propensity for fuels to break down when exposed to high temperatures is known as the fuel's thermal stability. In a similar manner to lubricity, this definition is not an absolute measurement of a fuel property, but rather an interaction between the fuel and its environment. The main fuel chemistry factor in the thermal stability performance of a fuel is the trace materials which are stripped out by increasing levels of hydrotreatment, the polar and heteroatomic species which exist at ppm or ppb levels within the fuel are removed.

The specification testing for Jet A/A-1 only requires the fuel thermal stability to meet a minimum standard and does not characterise the actual thermal stability limit of a fuel. The limit specified in the fuel specification is a ASTM D3241 Jet Fuel Thermal Oxidation Test (JFTOT) pass at 260 °C. The performance of the fuel may be above this limit and represents a fuel which performs above the minimum standard. In the pilot study conducted by Tucker et al. [29] the JFTOT breakpoint was recorded as a measure of the improvement in thermal stability as a result of hydrotreating (and reported as a function of sulphur content). This is shown in Figure 4.5 and clearly indicates a substantial improvement in the thermal stability performance and an increase in JFTOT BP from 260 °C to 300 °C.

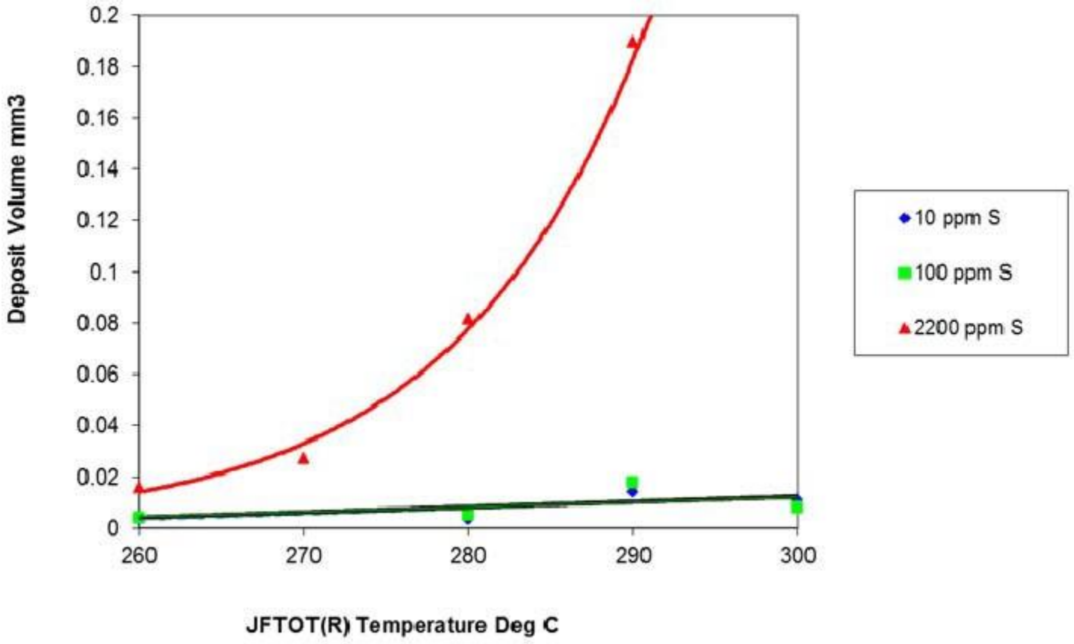


Figure 4.5: Change in thermal stability (deposit formation potential) as a result of successive levels of hydrotreatment to reduce sulphur content [29]

Storage stability

These heteroatomic species act as antioxidants which slow down the rate of degradation of the hydrocarbon when exposed to dissolved oxygen in the fuel. A measure of this autoxidation is test dependent but can be characterised as an induction time using the Petroxy test method (as shown in figure below). Hydrotreating these fuels strips out the heteroatomic species, resulting in more rapid degradation of the fuel, which can be an issue in fuel storage, resulting in fuels degrading beyond the limit of the specification and is the reason why hydrotreated fuels require antioxidant packages to be added to the fuel at the refinery [73].

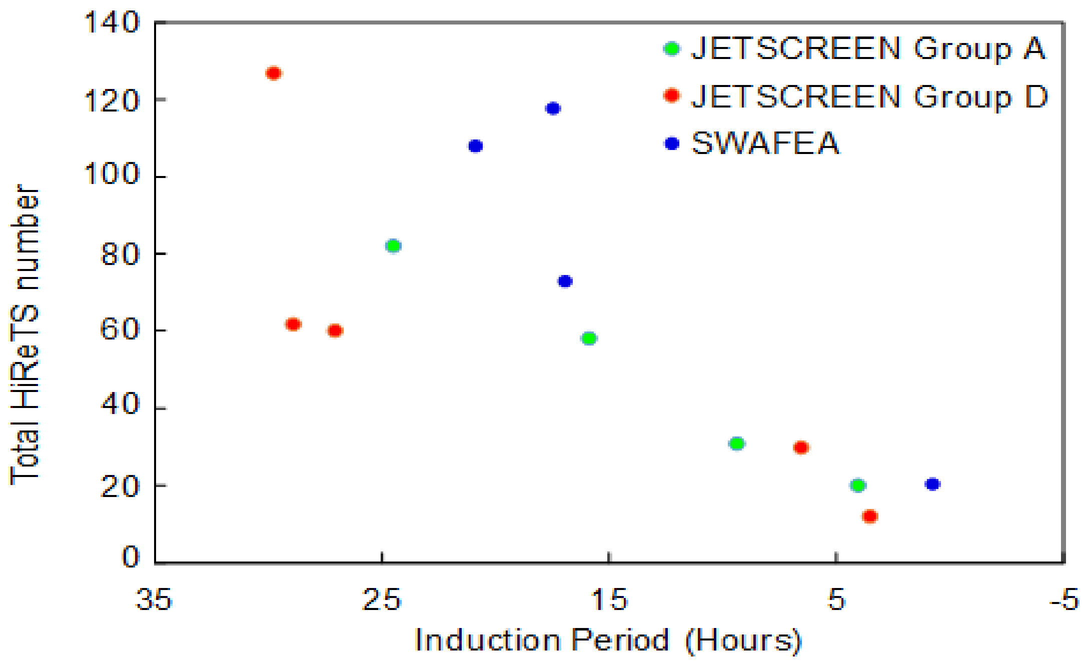


Figure 4.6 Thermal stability vs autoxidation more highly hydrotreated products low HiReTS number, low induction period [73]

The presence of these oxidised heteroatomic species results in the formation of deposit precursors which precipitate out of the liquid phase and form solid deposits which stick to surfaces in the engine core and ultimately cause changes in the engine performance which would require early engine overhaul. This can be characterised using the Total High Reynolds Number Thermal Stability (HiReTS ASTM D8611) number (as shown in Figure 4.6) and is proportional to the mass of deposit formed on a fuel wetted heated surface (higher Total HiReTS numbers = worse thermal stability performance). Highly hydrotreated fuels are less prone to this level of degradation as they do not contain the same heteroatomic species causing deposit and typically have significantly improved thermal stability behaviour. Highly hydrotreated fuels are required to be dosed with an antioxidant additive package to prevent this more rapid autoxidation to a maximum of 24.0mg/L in the final blended Jet A/A-1 fuel [9]. This would result in an increase in the cost of any highly hydrotreated fuel.

4.6. The impact of cycloparaffins

As part of the current study on the impact of aromatics on many fuel properties the issue of lack of, or indeed complete absence of, aromatics in most synthetic paraffinic fuels means that these fuels cannot be considered drop-in, and therefore are not compatible with current aircraft without the blending in of aromatics or "aromatic substitute molecules". This is mainly due to compatibility with certain elastomeric materials but also other properties such as energy density etc. However, as reported elsewhere in this report aromatics are known to increase smoke, particulate and increase radiative heat loading in hot end components. It has often been conjectured that cycloparaffins could act as a substitute for aromatics with the potential to induce seal swell and improve other properties without the emissions penalty. This study examines the risks and benefits of increasing the cycloparaffin content as a potential substitute for aromatics.

Generally held opinion (which this report examines and challenges) is that cycloparaffin content in the fuel could:

- In theory provide increased seal swell compared to aromatic free SPKs which comprise predominantly n and iso paraffins and therefore counteract the risk of seal leakage due the lack of swell of elastomeric seals which were designed assuming a typical swell level. Note that the main concern is with nitrile type seals (mainly O-rings) as they have a far greater swell response to aromatics versus fluorosilicone and fluorocarbon types. In this way cycloparaffins could act as a substitute to maintain compatibility.
- Reduce the inevitable increase in smoke, particulate, hot end radiative heat load etc that fuels with aromatics present tend to produce.

In summary the use of cycloparaffins could provide the required elastomer compatibility and some other benefits without incurring the smoke/particulate penalty that aromatics would. This could mean that a single synthesis process material could be fully drop-in, or, if blending with other components, the use of cycloparaffin compounds vs aromatics provides the combustion benefit.

The following review examines currently available data and information that may support the opinion that cycloparaffins could be used and identifies gaps in knowledge that would be required to further understand how such fuels would behave.

A CRC report ((CRC Project No AV-21-14) was carried out that reviewed the physical process of components within the fuel acting, in effect as a solvent and therefore causing swell, and calculation of swell rates by using the Hanson Solubility Parameter (HSP) concept [74].

The listed references represent most of the work as ASTM Research Reports on early work to qualify Sasol synthetic fuel blends [4], [40], [71], [75], [48], [76], [77], [78], [79], [80], [81], [82], [83], [84], [85], [86] and later out to evaluate the composition of synthetic blendstock materials to be included in ASTM D7566 [4]. The Moses reports [40], [71], [85] and the subsequent Lewis summary [86] collate much of this collective knowledge and understanding of primarily SPK type materials as regards their bulk and trace composition/composition, fit for purpose properties and performance. This dataset was examined specifically to assess how this data could be used to enumerate the hypotheses that cycloparaffins could be used a substitute for aromatics with regards to:

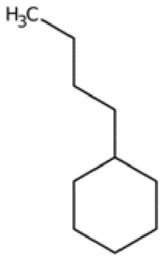
- Providing seal swell and therefore ensuring material compatibility in the absence of aromatics.
- Reduce overall smoke and particulate over aromatics and thus provide environmental benefit.

A short literature search was carried out to identify and examine any academic studies that addressed the question of the impact of cycloparaffins on seal swell. The main focus was the study of the impact on nitrile elastomers as the most “responsive” to swelling by hydrocarbons including cycloparaffins and aromatics.

4.7. Hansen solubility parameter

Several methods of modelling the interactions between liquids and elastomers have been proposed. One that has been examined recently in a study CRC Project No AV-21-14 [74] looked at Hansen Solubility Parameter (HSP). This formalises the interaction between liquids (as solvent) and materials (as solute) as elastomer swell is a mild version of solvation, or in other words likes to attract. This looked at various parameters that clearly showed on a scientific basis, by examining and matching molecular attributes, why aromatics will strongly swell certain elastomers and linear paraffinic molecules will not. This shows that cycloparaffins have some of the attributes of aromatics, namely relatively small molecular volume compared to n- or -iso paraffins. However, they lack the important dipole/polarity and hydrogen bonding properties that give aromatics their strong solvent properties. Therefore, Using HSP calculations predict that in general for cycloparaffins the propensity to enter the elastomer matrix is much weaker and therefore lower swell than the equivalent level of aromatics.

It is worth bearing in mind that molecules identified as “cyclo-” are a complex group with many permutations and most likely have a significant iso or n element attached if they are to be within the jet fuel boiling range (See aromatics measurement section). However, they are likely to behave more like cycloparaffins in this context. One example molecule to illustrate could include n-butylcyclohexane as shown in Figure 4.7.



Melting Point	-78°C
Density	818 kg/m3
Boiling Point	178°C to 180°C Flash
Point	50°C (122°F)

Figure 4.7: Example Cycloparaffin n-butylcyclohexane

4.8. ASTM data review

Some key caveats and limitations regarding the data available from both studies on conventional fuels and research reports on SPKs should be noted:

- Cycloparaffin content is not generally a required measurement for specification testing for conventional fuels. Their measurement and control is required for certain synthetic blends as defined in ASTM D7566 but again not a routine basis. Therefore, such data are only really available in fuel evaluation studies and therefore limited. One such study where this information was made available was the worldwide fuel survey by Hadaller et al. [14]. Note that this is now quite old, and the CRC is currently planning to carry out a fresh survey (as of 2023/4). Further:
- Early data on cycloparaffin content measurement methods that have been shown to be less reliable than believed so need some care in interpretation.
- None of the research report references were directly focussed on answering the question posed in this study i.e. can cycloparaffins be used as a substitute for aromatics. Therefore, information is limited due to there being no parametric test compared to programmes which would specifically address different levels of cycloparaffins with other parameters held constant.

In summary the key findings of a brief literature survey highlighted the following points.

The CRC Survey showed that conventional fuels could have between 0% and 60% cycloparaffins but most were between 20% and 40% . Note that synthesised cycloparaffins could have different range/distribution of carbon number and type compared to conventional fuels.

In general, SPKs thus far approved contain cycloparaffin typically between 0% and 10% but SPK/A may contain up to 20%, CHJ circa 30-40% and BB-SPK up to 30-40% (see ASTM D7566 Annexes).

Finished SPK blendstocks generally show a range of carbon numbered cycloparaffins from C8 to C16 so within the typical jet range.

As regards general jet fuel properties, cycloparaffins provide a slight increase in density and energy density per unit mass vs iso and n types and have good low temperature flow properties such as viscosity and freeze point.

Cycloparaffins can be present in the SPK or other synthetic materials by several routes dependent on the processes being used:

- Carry over without change from the raw material.
- Produced from the saturation of aromatic rings in the raw material.
- Production of cyclic rings from other paraffins from certain processes.

Thus, the presence or absence is raw material and process dependent. There is also a balance between yield and product purity requirements which dictates hydroprocessing severity which can alter cycloparaffin content.

Seal swell and performance impact

A review of numerous research reports has attempted to identify trends in swell of nitrile elastomers within the data presented – all comments below refer to nitrile-based elastomers and primarily O-rings. This is because nitrile is the most sensitive to aromatics levels in terms of swell and that other common O-ring materials such as fluorosilicone and fluorocarbon (Viton) respond much less or so low to be within experimental error. This review is to confirm or refute the generally held view that cycloparaffins do provide a level of swell and is expected to be more than n or iso but expected to be less than aromatics. It should be noted that other elastomeric and/or sealant type materials may also respond to aromatics levels.

The currently available evidence does not support the fact that these molecules cause significant nitrile swell. Note again that much of the work was based on comparing nitrile O-ring swell in both neat SPKs which generally had no aromatics but a range cycloparaffins (0%-40%) at various blending ratios up to 50% with convention fuels which generally had at least 16% aromatics before blending to ensure the 8% min. was reached after blending.

Findings that fail to show any effect under the test conditions and ranges of fuels tested show the following:

- In correlations of swell vs aromatics showed that all fuels sat essentially on the same line. In other words, the presence or absence of cycloparaffins in the various SPKs up to 40% has no discernible effect on the correlation.
- Studies which analysed the O-rings post-test by extracting the fuel components that were absorbed measured the partition coefficient, i.e. tendency of the fuel component to get into the elastomer – a higher number means a greater tendency to ingress the elastomer. Typical values (with some variation) were 0.2 for n and iso species, 0.2 for cycloparaffins, 0.5 for aromatics and 1.0 for multi-ring aromatics.
- Note that in these studies many of the fuel blends had conventional aromatics which may have competed with the cycloparaffins and suppressed their partition into the elastomers under test. However, it is clear that under these test conditions cycloparaffins tendency to cause swell is much weaker than aromatics. This seems contrary to the general belief that cycloparaffins will cause some swell over iso and n paraffins.

Overall, the evidence from the reports does not support the hypothesis that cycloparaffins will produce swell to the extent that they could substitute aromatics at concentrations within current experience based on conventional fuels. The reasons for this could include:

- The reports examined did not have sufficient testing, materials or conditions of the right focus to fully test the hypothesis (as this was not the purpose of the testing).
- Cycloparaffins will cause some swell, but it is much lower than aromatics (as expected) but not shown within the "noise" of other variables.
- Cycloparaffins will almost have to have multiple rings and/or n or iso type branches to ensure the molecules are within the jet boiling range. They therefore do not act purely as a single cycloparaffin ring molecule (larger molecular volume and less cyclo characteristics). Further, low molecular weight (low boiling range) cycloparaffin molecules may well cause more swell but would be excluded from jet fuels due to their high volatility/low boiling point.

The 8% min set in the D7566 specification for blending is not arbitrary and not just by a general consensus - Moses carried out a very comprehensive survey of conventional fuels for ASTM and determined that with 95% confidence all fuels at that time were above 8%. So while it was agreed (by formal vote at ASTM and therefore consensus) it was scientifically based in that it would keep FT blends within service experience. Also, since aromatics are a complex family, it also meant, again at that time, all the aromatics were what the industry knew and accepted within experience.

The Sasol work set the ground for the generic FT approval in D7566 via ASTM D4054 - neither of which existed in the form we know today when Sasol was approved. There are ASTM groups looking at drop in and non drop in 100%. But note the non drop in will not by default be approved on current aircraft but may be on a case-by-case basis for individual aircraft.

Combustion impacts

From a chemical perspective, although not always clear cut, there is a strong correlation between the chemical composition (specifically aromatic speciation) of fuels and their propensity to produce smoke or particulates. This is covered in greater detail in Chapter 5 for all fuel chemistries. Specifically, for cycloparaffins it would be expected that they have a lower smoke / particulate emission associated with their combustion – however the combustion hardware and fuel composition must be considered together to have a full understanding of the emissions performance.

Numerous test programmes reported in the above ASTM Research Report references clearly show that all aromatic free synthetics (SPKs) exhibited very low levels of smoke and particulate under a range of conditions. Importantly, this seems irrespective of the cycloparaffin content. But again, it must be emphasised that the data examined was not focussed on parametric testing of cycloparaffin content.

Thus, the evidence reviewed supports the hypothesis that the presence of cycloparaffins do not cause a significant increase in smoke level compared to SPKs with low or no cycloparaffins present. However, again note that none of the testing was actually focused on testing that hypothesis.

A brief study of an example of a more academic focussed research paper [14] and [87] provided some more insight into the seemingly contradictory belief that cycloparaffins can provide a useful degree of swell as a substitute of aromatics that wasn't borne out in the examination of the large body of ASTM generated data.

These papers all confirmed the key factors that determine how much swell individual cycloparaffin molecules can produce. Specifically:

- Pure cyclic molecules with a single or multiple rings i.e. with no paraffinic branches (substitution) e.g. Decalin will produce more swell that substituted cycloparaffin molecules, that is cyclic rings with n- or iso- branches attached.
- This confirms the fact that purely cyclic molecules have a relatively small molecular volume and may have some polarity. This polarity can increase with multiple rings and decalin has a relatively high swelling effect compared to other paraffinic molecules.
- The size and location of the substitution (branches) can cause steric hindrance and other effects that affect swell propensity.

As suggested above, lower molecular weight cycloparaffins have a greater swell propensity again due to their relatively small molecular volume allowing them to enter the elastomer matrix. A general rule of thumb from several of the papers suggest that 60-80% of decalin in the final blend (one of the highest swelling cycloparaffin within the jet boiling range) would be required to achieve the same swell of a typical aromatic containing jet fuel. Further, many of the types of cycloparaffin molecules found in SPKs would have a much lower effect and therefore would not produce enough swell even at perhaps 100%. Lastly, "spiking" a fuel with a single or narrow band of molecules is very undesirable due impact on other properties and would need significant evaluation to allow such a blend to be certified.

These research reports both support and explain the unclear correlation from the ASTM studies. That is that cycloparaffins will cause elastomer swell, but it is relatively low compared to aromatics, so in many cases not significant within other variables. Further, swell rates are very dependent on the configuration of the molecules. But in any case, the levels of cycloparaffins needed is much greater that the aromatics that they would need to substitute, and or, the highest swelling unbranched paraffins would be excluded from jet fuel due their volatility.

In general all the data examined shows that cycloparaffins do produce swell in elastomers, but the complexity of possible molecular species means that it is not a simple proposition. Further, whilst some modest swell may be produced over that of iso and n paraffins, achieving the required level as a true aromatic substitute at workable levels would be a challenge.

It is generally thought that cycloparaffins provide some level of elastomer swell and could be used as a substitute for aromatics in this regard, provide adequate energy density, and produce less smoke and particulate. This report examines this hypothesis by analysing various sources of data including a significant bank of data produced to evaluate potential blendstocks to be included in synthetic blends as per ASTM D7566 and a limited review of academic papers that took a more scientific approach.

A review of ASTM research reports showed that the amount of swell cycloparaffin molecules in the jet fuel boiling range produced was well below that of aromatics to the point where such effects were indistinguishable from other minor variables. But it was noted that these studies were not designed to directly address this question. Academic studies which included some parametric testing directly examining relative cycloparaffin swell rates and theoretical analysis supported and explained the findings of the ASTM reports review.

Experimental and theoretical examination confirmed that the amount of swell was dependent on:

- The molecule structure with in general multiple unsubstituted (no branching) rings providing the highest, single ring unsubstituted being lower and substituted rings (i.e. with paraffinic branches) being the lowest.
- Further, the relative location of the branches has an effect on swelling rates.

- Lastly the lower molecular weight cycloparaffins and therefore smallest molecular size gave higher swell rates.

Typical swell rates of Decalin (probably the highest swell rate molecule likely to present in the jet fuel range) needed to be present at circa 60%-80% concentration in the final blend to give the equivalent swell of a typical jet fuel. Further, lower swelling molecules would have to present at even higher levels.

Spiking of a jet fuel with Decalin to this level would have significant issues in terms of impact on other properties and would not meet current specification or fit for purpose requirement.

These findings explain why the general testing within ASTM studies of final blends and SPKs did not show a significant trend within the test programmes despite there being variations in cyclo concentration.

In summary, all the data examined shows that cycloparaffins do indeed produce swell in elastomers, but the complexity of possible molecular species means that it is not a simple or clear cut proposition. Further, whilst some modest swell may be produced over that of iso and n paraffins, achieving the required level as a true aromatic substitute at workable levels would be a challenge.

In other respects, combustion studies show that cycloparaffins do indeed reduce smoke and particulate levels compared to aromatics. And lastly, their physical properties would provide a means to produce fuels with density and energy density more in line with typical jet fuels.

4.9. Discussion

The impact of changes in hydrotreatment and aromatic content on the performance of fuel in the airframe, engine and combustor are varied and not necessarily complementary. It is challenging to create a consistent overview.

It is important not to look at fuel properties in isolation but understand the complexity and interrelation of all properties and their effects in parallel.

Sulphur, naphthalene, polar and heteroatomic species are removed by initial hydrotreatment of conventional fuels in order to reduce aromatic content to around 16%. This results in an improved thermal stability and in a reduction in auto-oxidation time as a result of species which act as antioxidants, trapping the available dissolved oxygen present in the fuel. Furthermore, at this level of hydrotreating, there is a marked reduction in the lubricity of conventional jet fuels as the polar species are removed from the kerosene cut, which results in poorer fuel storage stability. However, the opposite trend (non-linear) takes place with the removal of heteroatomic species which promote surface deposition in areas of the fuel system with high wetted wall temperatures. This does not account for potentially higher wetted wall temperatures resulting from changes in combustor heat release location due to changes in droplet break up highlighted earlier. These effects are summarised in Figure 4.8.

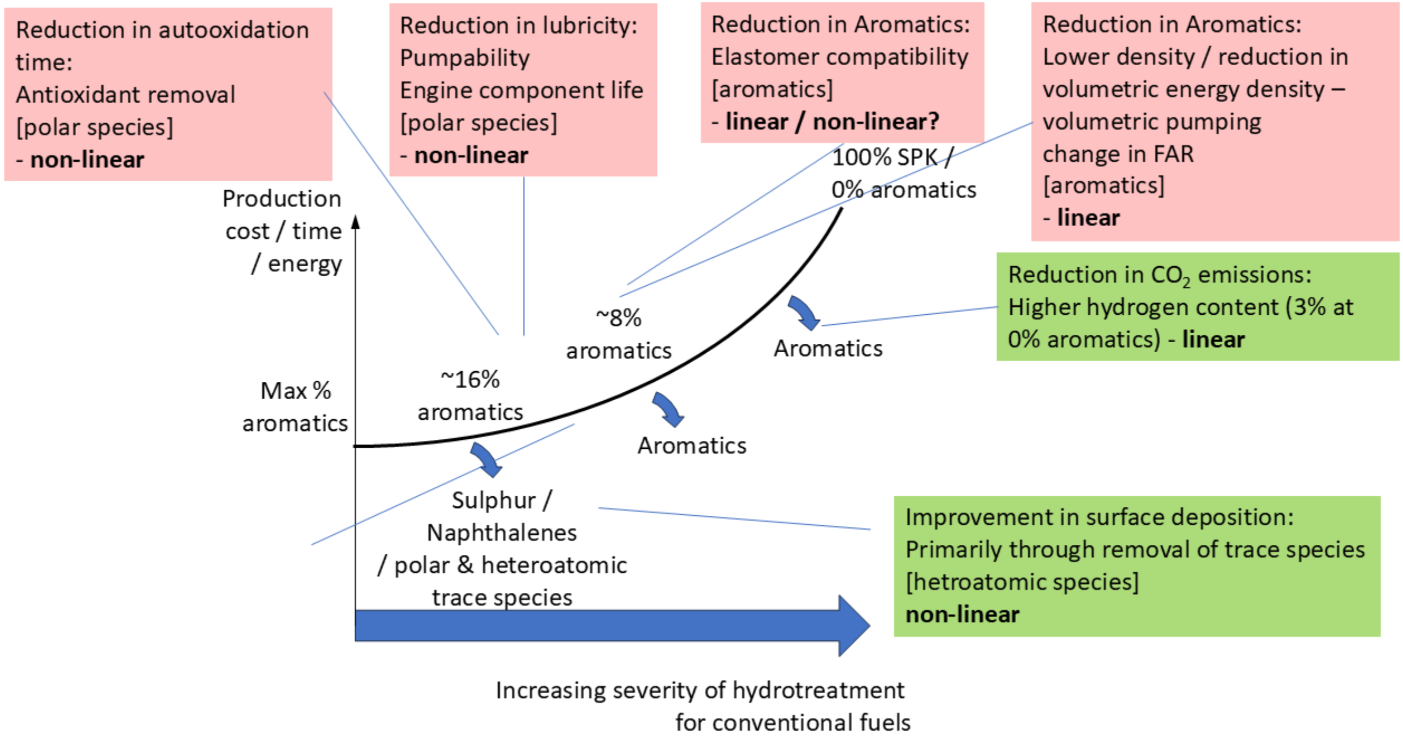


Figure 4.8: Overview of the impact of increasing hydrotreatment on fuel system performance

Additional hydrotreating of the fuel to the point the aromatic content reduces to below 8% leads to a reduction in the capability of ground handling and some aircraft systems with nitrile seals to swell effectively, risking leakage. Leakage of fuel is a significant hazard both from a safety and environmental perspective and should be avoided.

The reduction of aromatics below 8% is an ongoing discussion within the industry and has been since the advent of D7566 Annex 1 (FT-SPK). One significant constraint on reducing the aromatic content below 8% is that the response to aromatics in elastomeric components is very hardware and hardware age specific. For example, some new aircraft and engines have been designed to run on zero aromatics, but much older hardware is not capable. The exposure of elastomers to low aromatic content fuel is also a question of frequency; the difference between the occasional batch, continuous batch and switch loading (sequential high and low aromatic levels). In particular, the ground handling and fuel supply infrastructure will also need to be compatible with low levels of aromatics.

4.10. Research gaps

i. Lubricity vs thermal stability investigation for a range of hydrotreating steps with a set of representative fuels from a representative set of crude oils.

ii. Establish minimum aromatic content level for adequate seal swell. Currently an aromatic limit of 8% is considered an acceptable level of risk. The potential for leakage increases as the aromatic content drops below 8% towards 0%.

iii. Investigate the long-term impact of very poor lubricity fuels on engine components and working surfaces.

4.11. Conclusions

The below conclusions also hold for kerosenes containing synthesised aromatics providing the aromatics are well distributed across the boiling range. Control of aromatic content by ASTM D1319 appears to be adequate for the final fuel, although there may be limitations required on cyclo-aromatics, i.e., tetralins and indans, to assure the synthesised product has a composition that is typical of experience with conventional jet fuel [40]. [Note, confidence statements below are preliminary and are subject to further discussion and feedback]

1. In the absence of parametric testing on conventional fuels data /information from SPK studies has been used as this is a useful indication of impact of changes in aromatic content in conventional fuels. **(medium confidence)**

2. Lowering the fuel aromatic content to zero increases the fuel lower calorific value by up to 3%, due to the resultant increase in energy density per unit mass which in turn, lowers the aircraft fuel consumption and CO_2 emissions. **(very high confidence)**

3. Hydrotreating / hydrocracking to remove aromatics will also remove heteroatomic and polar species from the fuel, resulting in a reduction in lubricity of the fuel, reducing the life of engine components. **(high confidence)**

4. Lowered fuel lubricity would require correction through the use of approved additive packages which have risk and cost implications. **(high confidence)**

5. The impact of the removal of these species can be mitigated by blending highly hydrotreated fuels with straight run (CDU) fuels. Literature suggests 10-20% blend is sufficient although the level of trace species in fuels are falling due to the increase in hydrotreating, which may increase this blend requirement to higher percentages. **(medium confidence)**

6. The effect of removing aromatics from fuel will also have an impact on lubricity performance, however to a lesser extent than heteroatomic and polar species. **(medium confidence)**

7. The removal of trace species will increase the rate of autoxidation, requiring approved antioxidant additive packages to maintain fuel storage stability. **(high confidence)**

8. This would require the use of approved additive packages which have risk (incorrect usage and dosing) and an increase in fuel cost. **(high confidence)**

9. The removal of trace species will reduce the rate of thermal stability deposition. This may in time permit higher fuel system operating temperatures. Such engine design exploitation will mean engines will not be able to operate on conventional fuels with trace species present. **(high confidence)**

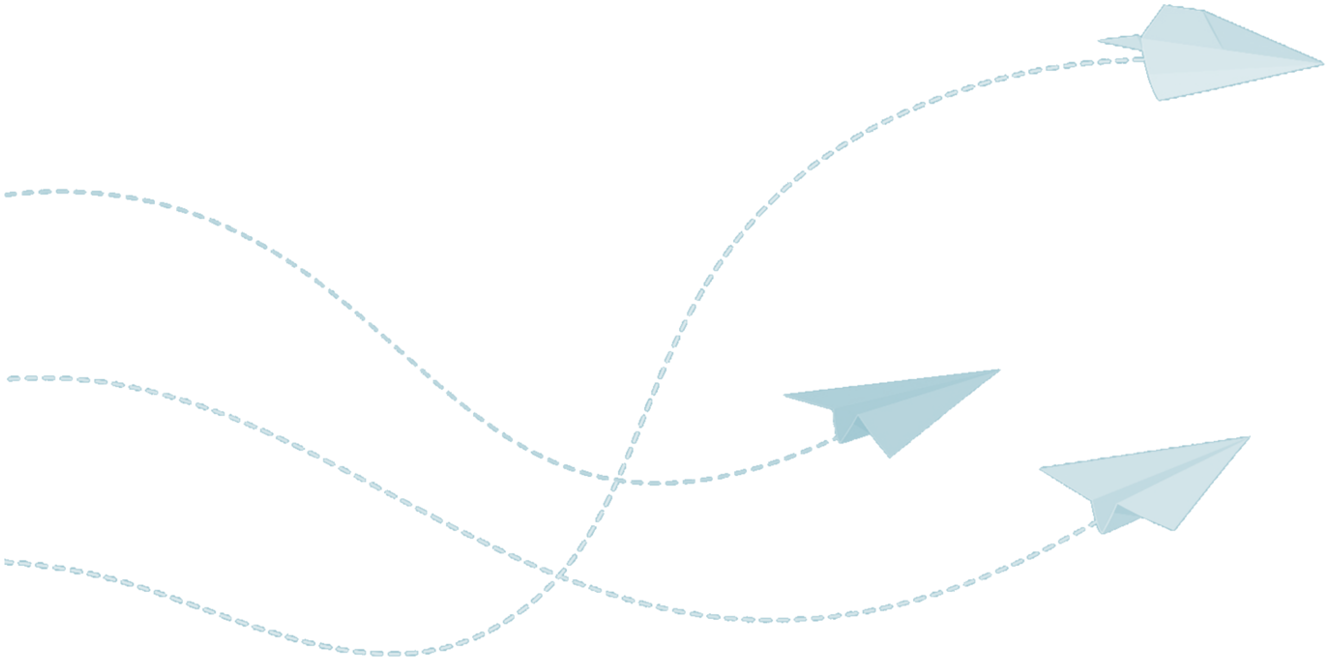
10. The presence of aromatic components in the fuel does not directly affect the thermal stability deposition propensity of the fuel. **(high confidence)**

11. The performance of certain low temperature elastomeric seals is dependent on aromatic content in the fuel. **(high confidence)**

12. The minimum level of aromatics for the adequate performance of low temperature seals is

currently considered to be at least 8% (by volume) and is the minimum level adopted in blending with synthetic fuels. **(medium confidence)**

13. The absolute minimum level of aromatics for seal performance is below 8%. **(medium confidence)**



5. Fuel atomisation, combustion and emissions

Summary

This chapter addresses the processes that result in the production of soot (non-volatile particulate emissions) through the fuel atomisation in the combustion chamber of the engine, the combustion process (which is technology-dependent) and the consequential emissions. Fuel atomisation – the process of forming a fine haze of droplets from a fuel injector – is affected by fuel properties, such as its density, surface tension, viscosity, and its ignition properties. Atomisation is also affected by hardware parameters such as the design of the fuel injector, delivery pressure, temperature, combustion chamber pressure, and air to liquid ratio. The process of soot formation is perhaps surprisingly poorly understood. This is because of the speed and severity (temperature, pressure) of the combustion process and its inherent difficulties in studying it in any other way than being empirical, i.e. observationally based. Our present understanding is that soot particles evolve from the formation of polyaromatic hydrocarbons (PAHs), their condensation and coagulation in sub nanometre-sized particles, a process called ‘inception’. Polycyclic aromatic hydrocarbons are a large group of organic compounds (many of which are carcinogenic), formed from the incomplete combustion of fuel. They are formed by two to six fused aromatic rings (in linear, cluster, or angular arrangements), consisting of carbon and hydrogen. The formation of soot from PAHs remains a topic of intense scientific study. Individual aromatic compounds have been studied in terms of their ‘sooting propensity’ in the laboratory. Apart from the atomisation aspects of the fuel, the engine combustion sub-system architecture has a large impact on soot emissions. Much of the current fleet of civil aircraft utilise so-called Rich-Burn, Quick-Quench, Lean-Burn (RQL) combustors. In contrast, ‘lean burn’ combustors are <5% of the present fleet but have the potential to dramatically reduce soot/particle emissions. In general, altering fuel composition can reduce particle numbers by tens of percent, whereas lean burn combustion can reduce particle numbers by orders of magnitude (factors of 10 or more). As such changing fuel composition could alter emissions on a fleet wide basis by a small fraction, conversely investing in renewal of the fleets engine combustion architecture to use lean burn technology over time would improve emissions significantly but would require engine refits to old aircraft or new aircraft with lean burn engines installed in place of RQL systems. Detailed studies of reduced particle emissions from the usage of SAF and semi synthetic blends with conventional fuel, which inherently have a lowered aromatic content, are available in the scientific literature and summarised in this chapter.

5.1. Introduction

In this section the physical processes required to form soot emissions are discussed and we consider the limitations of the combustion subsystem in terms of fuel aromatic composition.

We begin with a fundamental study on the formation of soot emissions by recording the historical development of the field to provide context. Next, we characterise the effect of various aromatic structures and further, various aromatic compounds in isolation and in jet fuel mixtures on sooting propensity.

Strong correlations are found between jet fuel aromatic content and sooting propensity as measured at the lab scale. In addition, a strong correlation is found between the degree of a compound or mixtures' HD and sooting propensity.

Next, we cover the atomisation of fuel detailing the effect of fuel composition on droplet size distribution followed by discussion around combustion of fuel in engine hardware, with consideration given to lean burn technology (limited data is available in the open literature on this topic). Consideration is given to the effect of fuel composition on operability parameters such as flashback, ignition stability and rumble.

Finally, a case study of nvPM emissions with low aromatic fuel taken from a NASA study is investigated in detail before studying the effect of emissions on a range of flight (cruise) and ground based emissions test data. Discussions and conclusions follow.

5.2. Fundamental studies of the formation of soot emissions

The combustion of jet fuel in aviation produces about a million tons of soot nanoparticles every year. These particles are harmful for the environment and human health. They can reduce visibility, increase the greenhouse effect, and cause cell damage. They also affect the formation of contrail cirrus clouds, which account for more than half of the aviation-induced radiative forcing (RF). Therefore, reducing or eliminating soot emissions from aircraft engines is a key strategy to mitigate their climate impact.

Soot formation is a complex process that depends on many factors, such as fuel composition, combustion conditions, and engine design. Soot formation has been studied extensively over the last five decades. The aromatic content of the jet fuel is a key factor. There is a strong correlation between the number of aromatics in the fuel and the particulate matter (PM) emissions. The aromatic content of the jet fuel is related to the number of carbon atoms in the fuel molecules and the C-H ratio. Aromatics are more resistant to decomposition and more prone to form soot precursors, such as polycyclic aromatic hydrocarbons (PAHs). Higher aromatic content leads to higher soot formation, especially in partially premixed combustion regimes. Aromatics also influence the size and shape of the soot particles, which affect their optical and physical properties.

Multiple fused aromatic rings, with two carbon atoms shared between adjacent rings, make up the molecular structure of polycyclic aromatic hydrocarbons (PAHs) [88]. PAHs can cause mutations in various organs by interacting with DNA, having mutagenic and teratogenic effects i.e. potentially resulting in foetal abnormalities. PAHs are also involved in the formation of combustion-generated particles. They initiate the soot formation process and take part in subsequent reactions, acting as precursors for soot as shown in Figure 5.1.

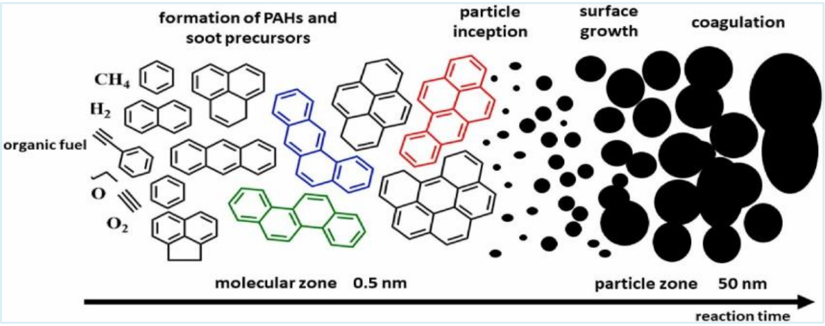


Figure 5.1: Schematic representation of soot formation [89]

In this review, the formation of soot particles will be summarised by delving into the mechanisms behind this PAH Growth and Precursors particularly the transition from gaseous PAH to solid carbonaceous particles via hydrogen abstraction and carbon addition, inception, surface growth nucleation, surface growth and coagulation/agglomeration mechanisms.

PAH formation: The formation of the first aromatic ring, such as benzene or phenyl, is a crucial step in the synthesis of polycyclic aromatic hydrocarbons (PAHs), which are composed of multiple fused rings. However, the exact mechanisms and pathways of this step are still under debate among researchers, and many different scenarios have been proposed based on experimental and theoretical studies, using various reactants and reaction types [90], [91], [92], [93], [94], [95],
[96] (see Fig. 5.2). Some of the most widely accepted reactions that can lead to the formation of the first aromatic ring are:

- C_2H_3 (vinyl radical) addition is critical for the initial formation of PAHs and soot [90]
- Reaction between a 4-carbon species (n-C_4H_5, n-C_4H_3) and 2-carbon species [91]
- 1,3-butadienyl radical (1,3-C_4H_5) addition to acetylene (C_2H_2), followed by hydrogen abstraction [92]
- The ion-molecule reaction between a formyl cation (HCO+) and acetylene(C_2H_2) [96]
- The reaction/addition between (C_2H_4) and cyclopentadiene (C_5H_6) [93]
- Self-reaction between 3-carbon C_3H_3 species [94]
- The addition of a propargyl (C_3H_3) to a 1,3-butadienyl radical (Wang and Ding, 2021)
- The addition of an ethynyl (C_2H) to 1,3-butadiene (1,3-C_4H_6) [96]

The carbon source and the environmental conditions affect the PAH formation and growth processes significantly, so a comprehensive approach is needed to understand the underlying mechanisms that takes into account all the relevant factors.

One of the main challenges in PAH research is to develop a suitable model that can explain how PAHs grow from smaller molecules. This topic has attracted many researchers from different fields and disciplines. There are many possible reactions that can lead to the formation of PAHs, depending on the types and concentrations of molecules and radicals in hydrocarbon flames [89] and is summarised in figure C.1 (Appendix C). Three main types of PAH growth mechanisms have been identified in the last four decades: acetylene additions, vinylacetylene additions, and radical reactions. In this section the impact of jet fuel aromatic components on PAH growth mechanism will be studied.

(i) The Hydrogen Abstraction and Acetylene or Carbon Addition (HACA) mechanism is a widely accepted model for the formation of polycyclic aromatic hydrocarbons from smaller precursors. It was first proposed by [92] and consists of two main steps: hydrogen abstraction from an aromatic ring, which creates a radical site, and acetylene or carbon addition to the radical site, which extends the ring (Figure 5.2). Acetylene, the main reactant molecule in HACA, is present in various kinds of aliphatic and aromatic flames, such as jet fuel. This shows its importance in PAH formation and its high probability of occurrence.

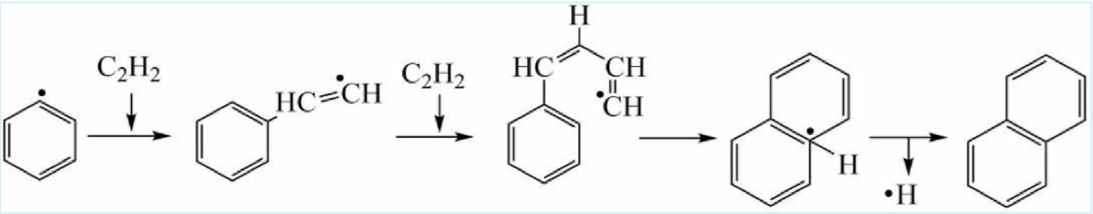


Figure 5.2 Bittner–Howard's reaction route for PAH formation [97]

(ii) One of the common methods for preparing aromatic compounds in the lab is the Diels-Alder (DA) reaction [98] which involves the combination of C_4H_6 and an C_2H_4 to form a cyclic compound. A similar reaction can also take place between C_2H_2 and a PAH suggesting that the benzogenic Diels-Alder mechanism is the main pathway for PAH growth, where C_2H_2 closes the bay region of PAH structures. The process involves two steps of the cycloaddition of acetylene to form the Diels- Alder adduct, and the elimination of hydrogen atoms. After the formation of the most condensed PAHs with all closed bays, larger particles can be formed via coagulation and agglomeration processes. VA (C_4H_4) is abundant in various types of combustion flames and therefore it can facilitate PAH formation reactions through hydrogen abstraction vinyl acetylene addition (Figure 5.3).

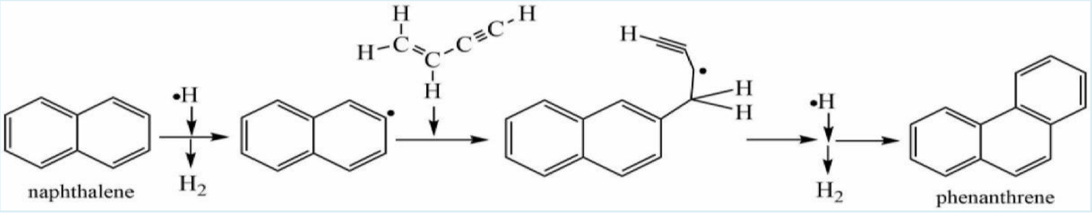


Figure 5.3 Diels-Alder-type reaction mechanism leading to benzo(a)pyrene formation [97]

(iii) Radicals play a key role in PAH growth. Depending on the type of radicals, they can react in different ways, using more or less stable carbon-based radicals. One of the simplest and most common radicals in jet fuel flames is the methyl radical.

Sooting tendency and chemical composition of the jet fuels

According to ASTM standard D7566-19 [4], jet fuels with synthetic components must have a minimum content of 8.0 vol% aromatics. Therefore, aromatics cannot be simply eliminated from jet fuels to reduce soot emissions when developing synthetic fuels. A better understanding of how aromatics and their molecular structures affect soot formation is essential for the development of alternative synthetic jet fuels. The sooting propensity of different aromatic compounds in jet fuels has been investigated.

There are several empirical routes to measure sooting propensity for example a commonly used, but non specification, threshold sooting index (TSI). A different way to estimate the sooting propensity of jet fuels is to use the soot threshold as a function of the fuel–air equivalence ratio (ɸ). This method measures the particle number concentration of soot in the exhaust gas of a premixed flat flame as the ɸ-value changes, that is, as the fuel fraction in the fuel–air mixture increases. Another useful correlation to compare the sooting propensity of different known jet fuels is based on the HD, introduced in Chapter 2 [1]. The concept of HD offers a valuable perspective for analysing the sooting tendencies of various fuels, particularly in the context of aviation. The HD number is a measure of the amount of cyclic and unsaturated molecular structures in a fuel, which are mainly responsible for soot formation compared to straight and branched alkanes. The HD-number can be used to predict the sooting behaviour of a jet fuel if its molecular composition is known. The experimental results of the sooting propensity will be compared with the predictions based on the HD correlation. This approach builds upon previous research [39] which demonstrated the ability to extrapolate particle emissions data for different fuels using HD values and a single reference measurement from an Airbus A320's V2527-A5 engine. The HD metric serves not only as a comparative tool but also as a predictive measure for assessing the sooting behaviour of jet fuels based on their molecular composition.

The sooting behaviour of various fuel blends was investigated experimentally by S. Richter et al. [39]. They used a crude oil based jet fuel (Jet A-1) and four alternative fuels, including two with aromatics (ReadiJet and Alcohol to Jet synthetic kerosene with aromatics) and two Alcohol to Jet Synthetic Paraffinic Kerosene and farnesane. They also prepared a synthetic paraffinic kerosene (SPK). The aromatic content was varied from 8.0 vol% to 16.5 vol%, and to 25.0 vol%, except for biphenyl which was limited to 17% Table 5.1 shows the structure and composition of the fuel components (including aromatics) used in this study. Figure 5.4 summarises the soot threshold (ϕST) results for the jet fuel and all of the surrogate fuels, based on either the aromatic concentration or the H-atom %mass. The experimental uncertainty for the soot threshold is ± 0.01. The results are more or less symmetrical because increasing the aromatic content reduces the H-atom amount in a fuel mixture. The different data spread between the aromatic concentration and hydrogen content depends on the SPK surrogate. The SPK surrogate does not affect the aromatic concentration, but it does affect the hydrogen content of each surrogate mixture with aromatics. The sooting propensity of the surrogates increases with the aromatic concentration, but not linearly. Adding 8.0 vol% aromatic to the SPK surrogate has a much bigger effect than increasing the aromatic from 8.0 to 16.5 vol% or to 25.0 vol%, respectively. The molecular structure of the aromatics matters more than their concentration for soot formation. Generally, the sooting propensity increases as:

mono-aromatics < cyclo-aromatics < di-aromatics

which agrees with a number of other investigators who studied the structural effects of various hydrocarbons on sooting propensity.

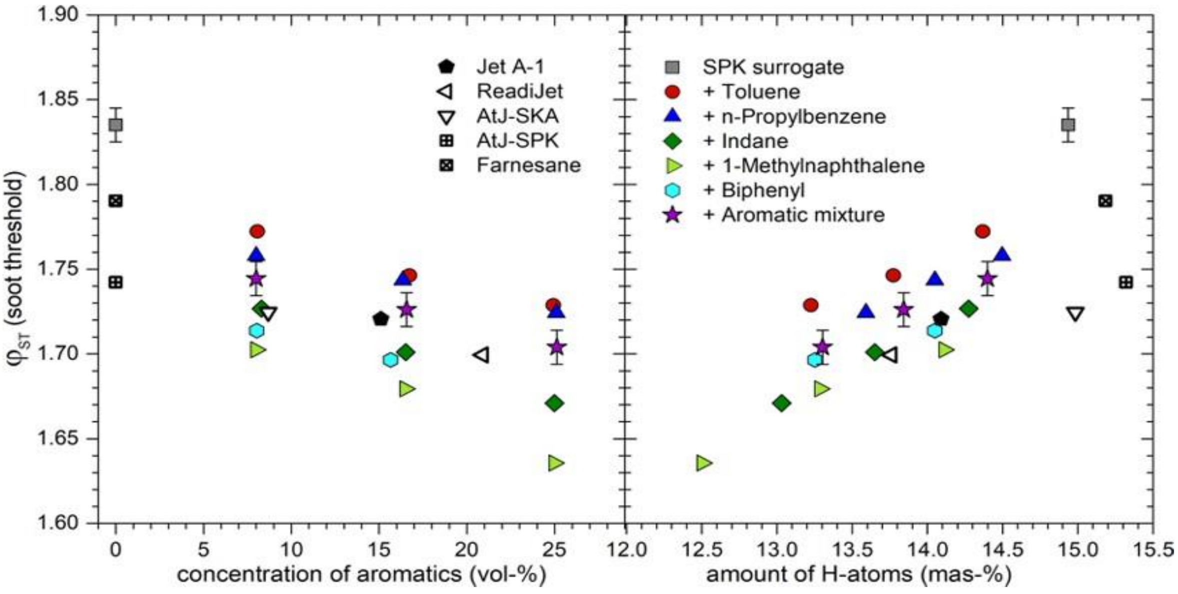


Figure 5.4 Sooting threshold vs aromatic concentration and H-atom mass % from [39]

Summary of important findings includes:

- The sooting propensities of the mono-aromatics toluene and n-propylbenzene are very similar because they have almost the same molecular structure. The only difference is that n-propylbenzene has a slightly higher sooting propensity (or lower soot threshold (ϕST)) than toluene, which could be due to its longer alkyl chain. Higher sooting tendency with longer side chains for other mono-aromatics has been observed by other investigators [39].

- Indane, a monocyclo-aromatic with nine carbon-atoms, has a sooting propensity between the mono- and di-aromatics. Indane and propylbenzene have the same number of carbon atoms, but indane has a lower H/C ratio of 1.11 (compared to 1.3 for n-propylbenzene) because of its fully cyclic structure, which leads to a higher sooting propensity. The di- aromatics, 1-methylnaphthalene or biphenyl have much lower ϕ-values for soot formation because they have H/C ratios of < 1 (0.91 for 1-methylnaphthalene and 0.83 for biphenyl).

- The aromatic mixture has a sooting propensity closer to n-propylbenzene and toluene than to indane or the di-aromatics, since the mono-aromatics are the dominant components.

- The soot threshold of the surrogate with 16.5 vol% aromatic mixture is close to that of Jet A-1, which has 15.1 vol% aromatics.

- The ReadiJet fuel has more aromatics and thus more soot than Jet A-1.

- The AtJ-SKA fuel has less aromatics but also more iso-alkanes, which are branched molecules that increase soot. The soot threshold of AtJ-SKA is similar to Jet A-1. The AtJ- SPK fuel has more branched molecules than AtJ-SKA and farnesane, which make it have more soot than both of them.

- Iso-alkanes, a branched structure increases the sooting threshold in comparison to straight n-alkanes confirming that the sooting propensity raises with the degree of branching in alkanes.

For the accurate determination of HD, it is essential to establish a theoretical formula for each fuel and fuel mixture under consideration. This process involves knowing the formula for mixtures like SPK surrogate and aromatic surrogate from the initial weight of pure components. The H/C ratio, a critical factor in this calculation, has been ascertained for Jet A-1, ReadiJet, and AtJ-SKA to be 1.95, 1.90, and 2.10, respectively. Utilising these ratios and assuming an average of 11 carbon atoms per fuel molecule, the theoretical formulae for real fuels were computed. Table 5.1 encapsulates the calculated HDs along with the theoretical formulations of each tested fuel and mixture. It's important to highlight that over half of the SPK surrogate consists of n- propylcyclohexane—a cyclic component—thereby increasing its HD compared to AtJ-SKA which contains aromatics. In figures 5.4 and 5.5, the estimated HDs are correlated with soot threshold (ϕST) and experimentally determined sooting propensities respectively, illustrating a direct relationship where a decrease in hydrogen content corresponds to an increase in HD. Accurate determination of the C and H contents in jet fuels is essential for estimating their higher heating value (HHV) without using a bomb calorimeter.

Table 5 1:Table of Jet Fuel blends aromatic content, mean chemical formula and hydrogen deficiency modified from [39]

Fuel			HD
SPK surrogate		$C_{9.05}H_{18.94}$	0.58
+Toluene	8.0 vol%	$C_{8.80}H_{17.59}$	1.00
	16.5 vol%	$C_{8.55}H_{16.28}$	1.41
	25.0 vol%	$C_{8.34}H_{15.15}$	1.77
+*n*-Propylbenzene	8.0 vol%	$C_{9.05}H_{18.28}$	0.91
	16.5 vol%	$C_{9.04}H_{17.61}$	1.24
	25.0 vol%	$C_{9.04}H_{16.94}$	1.57
+Indane	8.0 vol%	$C_{9.05}H_{17.95}$	1.07
	16.5 vol%	$C_{9.04}H_{17.03}$	1.53
	25.0 vol%	$C_{9.04}H_{16.13}$	1.97
+1-Methylnaphthalene	8.0 vol%	$C_{9.24}H_{18.09}$	1.19
	16.5 vol%	$C_{9.43}H_{17.21}$	1.82
	25.0 vol%	$C_{9.61}H_{16.37}$	2.43
+Biphenyl	8.0 vol%	$C_{9.31}H_{18.14}$	1.24
	16.5 vol%	$C_{9.56}H_{17.40}$	1.86
+Aromatic mixture	8.0 vol%	$C_{9.01}H_{18.07}$	0.98
	16.5 vol%	$C_{8.97}H_{17.18}$	1.38
	25.0 vol%	$C_{8.94}H_{16.34}$	1.77
Jet A-1		$C_{11}H_{21.5}$	1.25
ReadiJet		$C_{11}H_{20.9}$	1.55
Alcohol to Jet SKA		$C_{11}H_{23.1}$	0.45

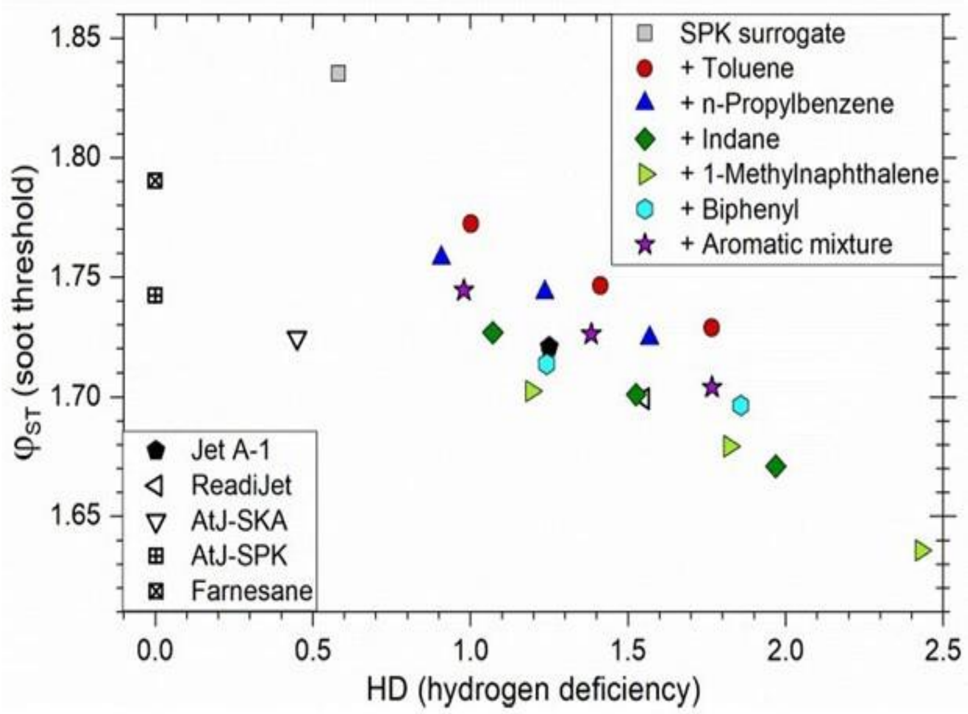


Figure 5.5: Sooting propensity vs. hydrogen deficiency, modified from [39]

Conclusion:

Further research on the sooting propensity of highly branched alkanes is essential. The correlation between HD and sooting propensity did not hold true for AtJ-SPK and AtJ-SKA. Iso alkanes and n-alkanes, as defined, do not contribute to HD. Despite these exceptions, both conventional (Jet A-1) and alternative jet fuels (such as ReadiJet) typically consist of various components. Therefore, HD remains a valuable tool for assessing the sooting potential of different fuels based solely on their chemical composition, eliminating the need for time- consuming experiments or model calculations.

Understanding and controlling soot formation in aero engines are essential for environmental responsibility and efficient engine operation. Further research and collaboration are needed to develop cleaner and more sustainable aviation fuels.

5.3. Definition of Emissions Index

The emission index (EI) is a dimensionless metric used to quantify the environmental impact of various processes. Specifically, it represents the mass of pollutant emitted (e.g. NO_X) per unit mass of fuel consumed and it is mainly used for trace species.

Thus, for the complete combustion of CH_4, the emissions index of CO_2 would be $EI_{CO} = 4$:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \tag{5.1}$$

Multiplying out by molecular masses:

$$(12+4) + 2(32) \longrightarrow (12+32) + 2(2+16) \tag{5.2}$$

i.e. 16 grams of CH_4 will generate 64 grams of CO_2, yielding $EI_{CO} = 4$ grams of CO_2 per gram of CH_4. The EI is often reported as g emission per kg fuel.

5.4. Atomisation / delivery of fuel in engines

In order for combustion of a liquid fuel to occur, it must first flow into a film, form ligaments, then droplets, evaporate into a gas (liquid fuels don't burn) and mix with surrounding oxygen in the correct quantities (see Limits of flammability section), at sufficiently high temperature and ignite to sustain a chemical reaction at a given pressure.

Atomisation performance describes the ability of a given fuel to form droplets in a controlled manner with a given injector and combustor at the relevant operating conditions prior to combustion. In practical terms this necessitates that droplet size distribution and spray cone angle should fall within requirement limits to ensure the correct placement of the fuel spray and thus allow ignition to take place in the correct zone of the combustor. This is important at normal conditions to ensure efficient and complete combustion. There is also the challenge of ensuring combustion under low power or relight conditions. The correct fuel placement across the range of operating conditions is therefore required to prevent poor fuel and air mixing resulting in misplacement of the flame and/or instability of excessive emissions etc.

The first step in this process is to form a controlled spray of atomised fuel droplets as described by Lefebvre in [99]. Once formed, fuel droplets evaporate in the surrounding fluid, forming vaporised (gas phase) fuel which can be mixed readily with oxygen in the air and ignited to liberate the fuels chemical energy, releasing heat into the engine's compressed working fluid, air. As such, droplet size should be small enough to allow the liquid fuel to fully evaporate and burn in the correct portion of the combustor to avoid generating uncontrolled combustion emissions. Droplet size is usually characterised in terms of the Sauter Mean Diameter (SMD), the statistical mean of the droplet cloud generated by a fuel injector, although other measurements can be made to determine the probability density function of droplet size (the statistical likelihood of a droplet being a given size). Droplet size is controlled by a raft of injector, engine and fuel specific parameters:

Hardware parameters:

i. Fuel injector (atomiser) architecture and the size of key geometric features.
ii. Fuel delivery pressure
iii. Air delivery pressure, pressure loss and velocity across the injector
iv. Air to liquid ratio
v. Operating temperature and pressure of the combustor

Fuel parameters:

vi. Fuel density
vii. Fuel surface tension
viii. Fuel viscosity
ix. Ignition delay / Cetane number

As such, a change in fuel aromatic content can change spray droplet size due to the physical property changes discussed in Chapter 3 for a given engine and injector as a function of fuel density, surface tension and viscosity. The impact of this change on fuel emissions will depend on the operating conditions provided to the injector and combustor by the engine and the choice of injector design.

There are many gas turbine fuel injector designs but as a broad generalisation these fall into two main types. Pressure jets, where the fuel pressure and a relatively small orifice provides the primary kinetic energy to produce atomisation, and these are found on older engine designs but also used widely on Auxiliary Power Units (APUs) since they are very compact. Larger and more modern gas turbine prime movers tend to have air spray injectors where the air flow mixing with the fuel by complex air/fuel intermixing zones is the predominant source of kinetic energy. In general since the pressure jet relies on the fuel for spray formation, they are more sensitive to fuel physical properties than air spray designs. Each design has its pros and cons for each application and note that modern gas turbines may have complex injector designs combining both pressure jet and air spray elements to provide optimum fuel placement under all conditions.

Moses et al. [100] note a reduction in fuel droplet SMD measured downstream of a pressure at Auxiliary Power Unit (APU) gas turbine start up conditions when switching between conventionally sourced petroleum-based Jet A and Sasol SPK, which is analogous to a highly hydrotreated conventional fuel [100]. Conventionally sourced Jet A used here was composed of 22.9 % aromatics by volume, compared with 10.9% by volume for the Sasol SPK test fuel.

This change in SMD can be seen in Figure 5.6, indicating that droplet SMD for Sasol Fully Synthetic Jet Fuel (FSJF) will be approximately 25% less across the population of droplets at low pressure (2 bar injector dP) with a smaller benefit seen at higher pressures, reducing further with increasing pressure drop. Note that this finding is linked specifically to a pressure atomiser used in a Honeywell APU which would provide power for instrumentation and engine start up at airports. These APUs can be found in the tail of civil airliners and run for long periods of time on the ground to provide instrumentation power before the main engines have been started. APU are also used as a safety power back up on certain aircraft, particularly on extended range twin engine operations (ETOPS) so may also be operating during descent and landing and ability to start at the end of cruise following cold soak and at high altitude is a safety critical requirement.

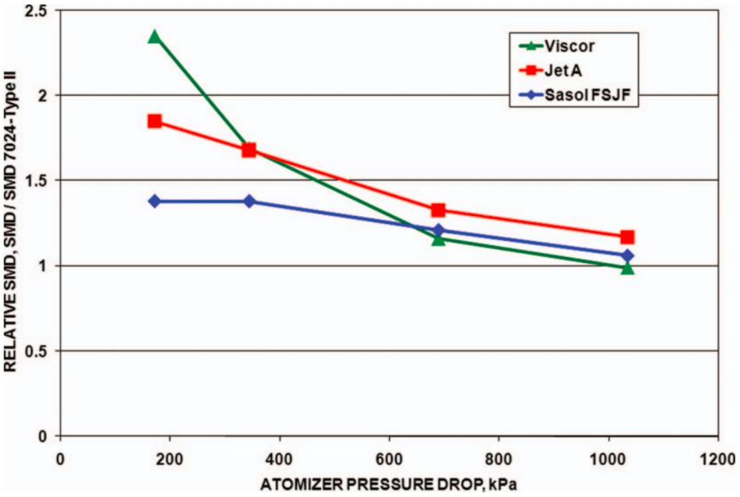


Figure 5.6: Atomisation of Sasol FSJF compared with Jet A at -40 in a pressure atomiser [100]

Some injector geometries will be less sensitive to change in fuel composition and some engines will likely provide conditions which are further away from the low temperatures and pressures which augment the effect of different fuel composition (higher compression ratios with high temperatures and pressures) as seen above. Moses et al show in Figure 5.7 that no significant change in SMD was evident for air blast atomisers tested [100].

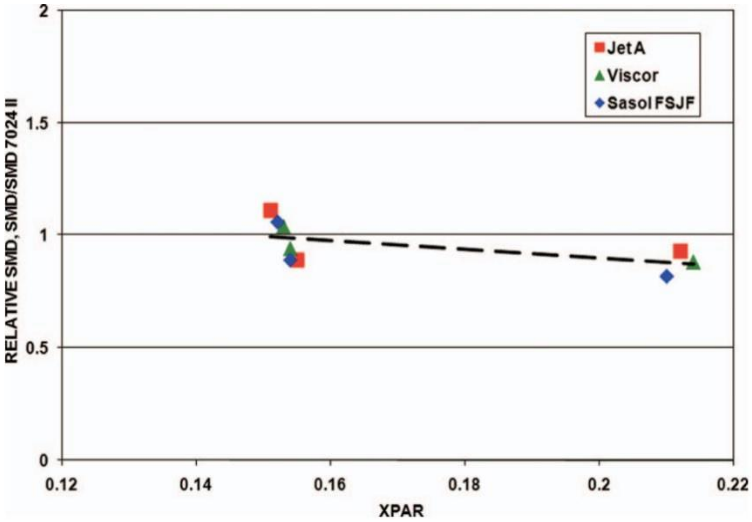


Figure 5.7: SMD measured downstream of an air blast atomiser, relative to standard test fluid [100]

[100] states that there was negligible change of spray cone angle at the start up conditions measured for Honeywell's APU pressure atomiser. Spray cone angle is defined as the angle between the extremities of the fuel spray cone, measured in plane with the centreline of the atomiser. Changes in spray cone angle affect fuel patternation and operability parameters such as ignition stability and turbine inlet temperature distribution. in addition to as a result. This may not be the case for air blast atomisers. Honeywell concluded that there should be no change to start up behaviour based on this change in fuel with 50% less aromatic content.

Furthermore, Kannaiyan and Sadr [101] find that Natural Gas Synthetic Paraffinic Kerosene (NG SPK) exhibits a marginally smaller droplet diameter than Jet-A when sprayed from a pressure swirl atomiser, but that the droplet distribution appears to be somewhat skewed about the similar Sauter Mean Diameter (SMD) towards smaller diameters [101]. This feature was evident in the results at both 1 bar and 9 bar ambient gas pressures and nozzle pressure drops of 3 and 9 bar gauge, as shown in Figure 5.8 and is a function of lower density, surface tension and viscosity.

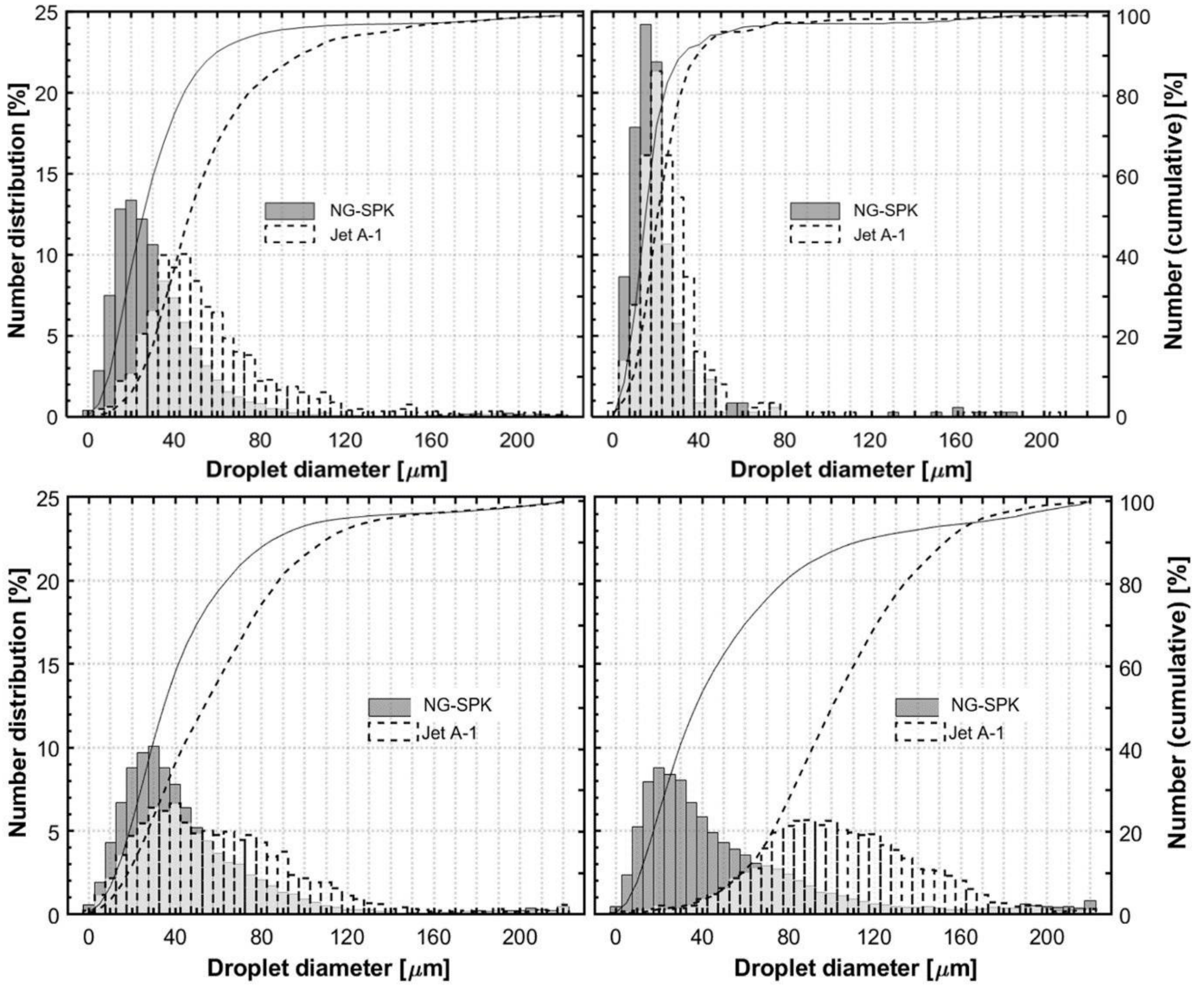


Figure 5.8: Comparison of Jet A-1 with NG-SPK fuel atomisation at a range of ambient gas pressures and injector pressure drops.

(Upper left ambient gas pressure 1 bar, injector differential pressure 3 bar; Upper right, ambient gas pressure 1 bar, injector pressure differential 9 bar; Lower left, ambient gas pressure 9 bar, injector pressure differential 3 bar; Lower right ambient gas pressure 9 bar, injector pressure differential 9 bar) [101]

Spray patternation describes the location (cone angle of the spray cone formed), droplet size and density of the fuel spray in the combustor. Experiments are usually carried out at atmospheric conditions to determine spray cone angle and droplet size with optical measurement techniques to compare changes in injector design. Size and frequency of droplets in addition to cone angle can change with the downstream distance from the injector.

Based on the reviewed literature, air-blast atomisers show no trend in droplet size between conventionally sourced Jet–A and FT synthetic jet fuel with low aromatic content. Conversely, however pressure swirl atomisers do exhibit a change in droplet size, with FT Synthetic jet fuels producing smaller mean diameter droplets and a larger distribution of small droplets. This trend increases with reduced operating power in the APU tested. Hicks et al [102] note that GE TAPS injectors demonstrate changes in fuel atomisation with lower aromatic content fuel, JP-8 evaporating faster than low aromatic HRJ fuel during low TRL tests. The authors also state that this may be due to measurement uncertainty, hence further research is required. Additional research is required to determine whether this result is applicable at large engine scale across the full fleet. This research should cover Rich Quench Lean Burn (RQL, further explained in section 5.6) combustors and the most modern engines using novel injection technologies using different injector architectures.

To summarise, fuel composition changes that will change physical properties will impact on atomization which can vary depending on fuel injector design. OEMs should consider if testing their equipment using conventionally sourced fuels with reduced aromatic content, and corresponding physical property shifts is required to determine the effect (if any) of this change.

5.5. Combustion of fuel

The combustion process takes hot fuel from the fuel management system of the aircraft and is mixed with compressed air from the engine, to form a reliable, repeatable mixture which readily combusts in a safe, controlled manner to deliver thermal energy to be extracted by the turbine stage of the gas turbine.

Continuous and stable combustion under normal operating conditions is a given. But this process must be controlled in order to maintain ignition stability at high altitude and in more challenging conditions such as in the event of flame extinctions due to adverse climatic conditions. As such, it must be possible to re-ignite the flame at highly altitude, low pressure extremely low temperature conditions which require a highly volatile fuel to allow ignition to take place, as liquid fuels only ignite once sprayed, mixed with mildly heated air and vaporised then adequately mixed prior to chemical reactions taking place.

Furthermore, viscosity, fuel volatility and density affect a fuel’s ability to evaporate and ignite at engine operating conditions across the engine’s operating cycle. These properties in turn affect operability parameters such as relight and lean blow out (LBO) as well as combustion thermo- acoustics (rumble) which can cause unwanted acoustic tones and noise pollution around airports. At worst rumble can destroy an engine’s combustion chamber due to large amplitude thermo- acoustic instabilities, if not correctly designed out during engine development and testing.

The Cetane number, as discussed in Chapter 3, is an indication of the fuel’s ignition delay which is in turn an indicator of a fuel’s reaction rate and activation energy at a given condition. Changes in fuel cetane number will also change a fuels thermos-acoustic response which will be driven differently in each different combustion hardware / operating condition combination.

Fuel filming, ligament formation, droplet atomisation, droplet break up, evaporation and reaction are all key stages to combustion. Each stage must be considered to determine the effect of a change in fuel composition and each of these stages are dependent on operating conditions as well as combustor hardware factors.

Each of these factors are essential to maintain proven, reliable, and safe power delivery to take place, allowing passengers to trust aviation as a safe means of transport whilst maintaining emissions and noise requirements across all cycle conditions. Fuel composition, properties and subsequent performance are critical to ensure each of these aspects are optimised. As a result, changes to fuel composition and performance must be quantified, evaluated and constrained within specific requirement limits.

5.6. Combustor hardware and aromatic content

Introduction to hardware

The majority of the current in-service fleet of aero engines operate with Rich-Burn, Quick-Quench, Lean-Burn (RQL) combustors, using well understood technology to maintain a robust, stable flame across the aircraft flight envelope. Rich burn fuel injectors inject fuel into the combustor's fuel rich primary zone, prior to dilution with quenching air to reduce the flame temperature and curtail thermal NO_x emissions. Addition of large quantities of secondary air to a rich flame rapidly reduces the flame equivalence ratio from ~ 1.5 to ~ 0.5 as can be seen in Figure 5.9 [99]. This quick quenching of the flame reduces residence time of the combusting mixture around the equivalence ratio close to unity which would promote a high temperature flame and generate high concentrations of thermal oxides of nitrogen. It should be noted that injector and combustor design have to balance two conflicting requirements i.e. having a zone with sufficiently high temperature and residence time to ensure complete combustion (particularly for the more difficult aromatics fraction) vs. such high temperature and time producing NO_x.

Fuel aromatic content reductions below the current average of 16% will change fuel reactivity, reducing the ignition delay (see Chapter 3 for comments on Cetane number for further detail). As such, OEMs are currently discussing whether combustion system design rules could be changed, allowing for simpler combustion systems if the high temperature primary zone in RQL combustors is not required.

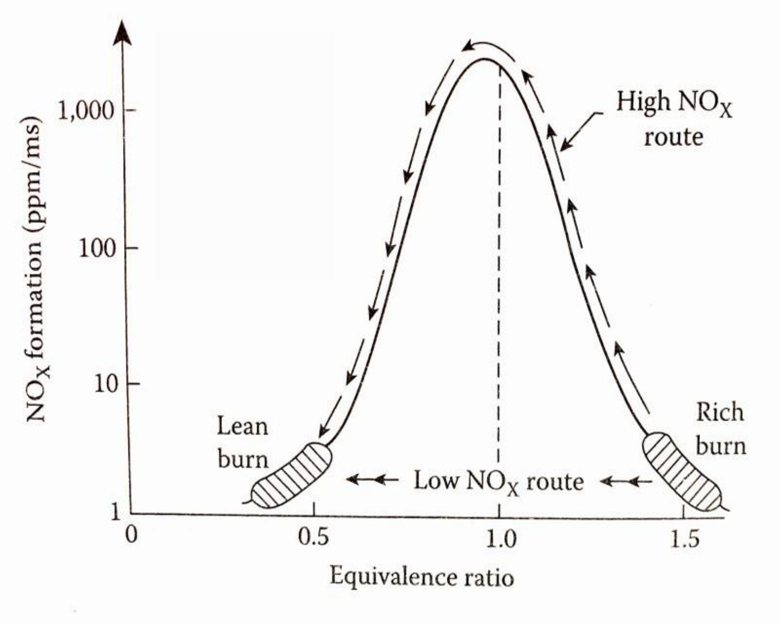


Figure 5.9: Effect of Equivalence Ratio on rate of NO_x formation. RQL technology follows the Low NO_x route by injecting a high air flow rate downstream of the stable, fuel rich primary combustion zone [99]

Walker et al. [103] illustrate conventional RQL and lean burn combustor architectural cross sections in Figure 5.11 a) and b) respectively. It can be seen that, in the case of RQL combustors, approximately 30% of the air passes through the fuel spray nozzle to allow adequate air for mixing and combustion of fuel. The remaining 70% of air is split between passing through the inner and outer liner flows. Some of this air is used for liner cooling while the majority of this air is used to cool the combustion process through mixing ports in the secondary zone in order to reduce thermal NOx emissions as shown in Figure 5.10

Lean burn combustion systems are already in service in <5% of the market, so need to be considered for any safety case where fuel chemistry is changed. This lean burn technology is illustrated in Figure 5.10, b) [103]

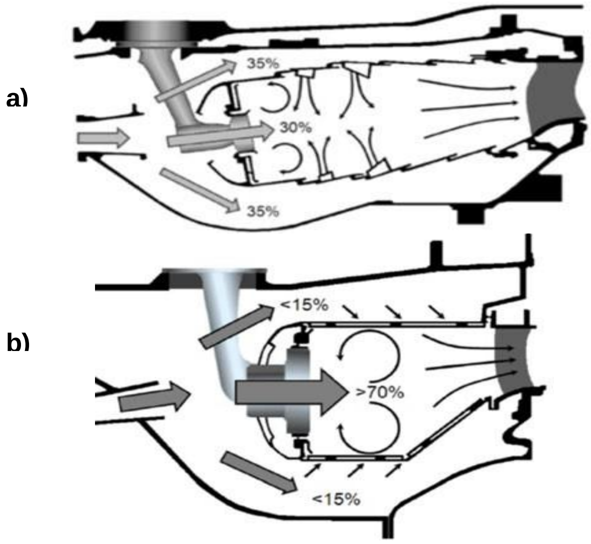


Figure 5.10: a) Conventional rich burn combustor architecture and b) Lean burn architecture adapted from [103]

Lean burn combustors achieve NO_x reductions by generating a leaner global mixture of fuel and air when operating at higher power conditions. This is achieved by using 70% of the combustor delivery to mix with fuel in the combustor head and the remaining 30% to cool the combustor walls [103]. Lean burn combustors maintain stable ignition by running a fuel rich pilot injector at low power conditions and pilot and lean main injector simultaneously at high power conditions after ‘staging in’ the mains fuel circuit. This technology uses a variety of injector technologies such as lean direct injection (LDI) and lean premixed prevaporisation (LPP) as described in the work of Lieuwen and Yang) [104]and Lefebvre and McDonnell [105] which pose different risks to RQL combustion technology and need to be assessed accordingly.

It should also be mentioned that lower bypass ratio military engines are also fuelled with Jet A-1, including their afterburner systems. These combustion system architectures are deemed beyond scope for this report as the focus is on civil aviation and indeed, much of the information surrounding their design and operation is not available in the open literature. As with civil engines, it should be noted that fuel aromatic content will likely impact key performance parameters in military engine design such as thermo-acoustic instability (afterburner screech), in addition to the impacts identified in this report.

Operability

This study aims to determine the effect of ‘drop in’ low aromatic content fuels on combustor operability in the existing fleet of aero engines. The purpose of this section is to determine the potential risk presented to existing combustor hardware life and operability if the standard specification for Jet A-1 is changed to lower the aromatic content and this takes composition and/or properties outside the norms for existing conventional fuels.

Please Note: this section is an introduction to the risks associated with fuel chemical change effects on combustion hardware and is by no means exhaustive. Further work at the range of TRL levels and across all aero engines (by engine OEMs) would be necessary to guarantee safe, reliable and cost-effective flight for passengers and operators.

1. **Limits of flammability** - Li et al [106] report absolute flammability limits for low aromatic HEFA and FT-IPKs in comparison with conventional Jet A at atmospheric and sub- atmospheric conditions in quiescent premixed conditions, finding that the absolute lower flammability limit of low aromatic fuels was leaner than for conventionally sourced Jet A at the conditions tested.

2. **Flame speed** - Kumar et al [107] study the effects of flame speed and flame extinction limits in FT-IPK with low aromatic content and conventionally sourced Jet-A. The authors find that the extinction limits for FT-IPK are marginally lower than that of Jet-A, but that the extinction limits occur at higher rates of flame stretch in turbulent flows.

3. **Ignition performance** - Moses et al. [100] tested ignition performance (ignition stability and relight at simulated high altitude conditions) at TRL 6 using low aromatic Sasol FT-IPK and conventional Jet A-1 in a full annular combustion test rig. Test data showed equal performance between FT-IPK and Jet A-1 at all conditions other than the toe of the high altitude envelope. The report stated that further work was necessary to understand the differences in ignition stability at high altitude relight conditions. Further testing at Rolls- Royce Derby Plc by Fyffe et al. [108] showed no marked difference in relight at the conditions tested in a twin sector lean burn combustion system at TRL5. Perhaps the difference can be attributed to flame speed changes rather than flammability limits, as points 1) and 2) of this chapter would suggest. This warrants further research to fully understand the issues surrounding ignition performance at the limit of the high altitude envelope.

4. **Flashback** - Flashback can be described as a rapid pressure rise combustion event associated with spontaneous ignition of fuel across a large volume, typically in lean premixed prevaporised (LPP) injectors [99]. The effects of flashback in aeroengine combustors are catastrophic and as such warrant significant development in understanding of this risk prior to changing fuel specifications.

   Lieuwen et al. [104]. Lim et al. [109] study the effects of fuel chemistry and equivalence ratio on flashback in premixed alkane-air flames a laboratory scale test rig, finding that differing fuels presented higher flashback risk at lower air mass flows depending on the fuel chemistry, with fuel chemistry and equivalence ratio determining the flashback mechanism. No studies were identified addressing flashback of jet fuel with varying chemical composition in simulated or real combustor hardware or realistic operating conditions. This risk should be assessed thoroughly prior to changing drop in fuels, as engine operating parameters in LPP lean burn systems are carefully programmed to avoid flashback events with current fuel chemistry only.

5. **Combustor liner life** - Aeroengine combustor life is dependent on the liner wall temperature. This is in turn, dependent on the flame emissivity which is dependent on the C/H ratio of the fuel, or hydrogen content as shown in Figure 5.11. This effect is accentuated where combustor design necessitates

a rich primary zone as is the case in RQL combustors which generate hotter and yellower rich flames [99].

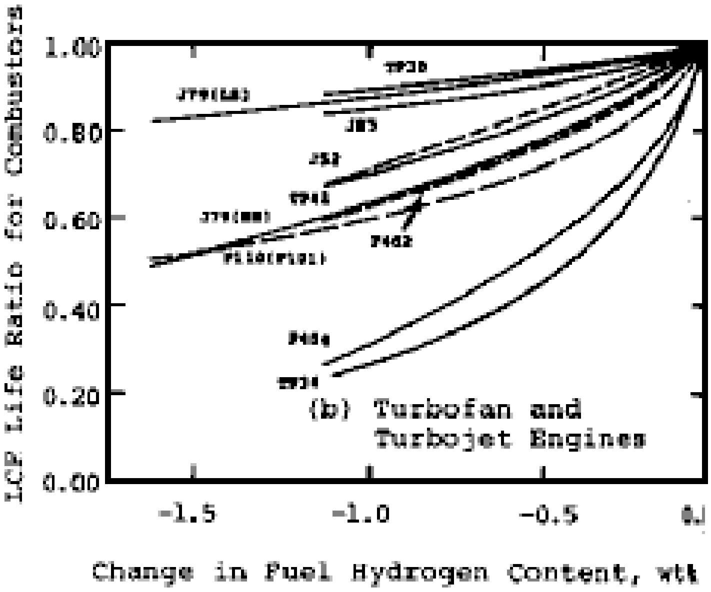


Figure 5.11: Effect of change in hydrogen content on combustor LFC ratio [110]

Studies have been carried out by several authors finding that increasing jet fuel hydrogen content reduces flame radiation due to reducing carbon content, increasing combustor liner life due to reduced flame luminosity [111]. The effect of fuel hydrogen content on in service combustor life by Moses and Karpovich [110] across a range of turbofan and turbojet engines, confirming that lower fuel hydrogen content results in reduced combustor liner life.

5.7. Emissions performance

RQL combustor PM emissions

At present, aircraft gas turbine engines almost exclusively rely on hydrocarbon fossil fuel as the main source of energy to generate thrust and power. The combustion of these fossil fuels by aircraft engines result in the production of various pollutants including both carbon dioxide (CO_2) and non-CO_2 components, including nitrogen oxide (NO_x), particulate matter (PM), water vapour (H_2O), carbon monoxide (CO), sulphate particles, and unburnt hydrocarbons (HC). At cruise altitudes under specific atmospheric conditions characterised by high humidity and low temperatures, both the ambient and emitted H_2O can also condense and freeze onto the PM found in the exhaust plume to form contrail ice crystals. When the atmosphere is supersaturated with respect to ice, these contrails can persist, spread across large swathes of the sky, and contribute to anthropogenic climate change. As the aviation fuel composition and properties are known to influence the aircraft CO_2 and non-CO_2 emissions, modification of fuel composition has been suggested as a means of mitigating these effects.

Parametric studies on conventional fuels with varying aromatic levels are very scarce. However, there is a large bank of work that has been done looking at the impact of SPK blends which in effect dilute the aromatics. To provide some indications of the likely impact of reducing aromatic content, these studies are cited as a surrogate for the potential impacts of increased hydrotreating resulting in lower aromatics.

Our focus is on compiling data from previous experimental campaigns, particularly those that measured

PM emissions from aircraft gas turbines with different fuel composition and properties. The following sections provide an overview of the aviation fuel composition, the impact of fuel aromatic and sulphur content on aircraft particle number emissions, the influence of fuel properties on contrail formation and the associated young contrail properties, the effectiveness of fuel hydrotreatment in reducing the aerosol and contrail climate forcing, and a summary of the potential implications from fuel hydrotreatment.

For example, one of these campaigns is reported in Bulzan et al [112] and summarised in Table C.1 (presented in Appendix C), who studied the effect of changing fuel composition on PM emissions. Fuels tested ranged from conventional JP-8, the military equivalent of Jet A-1, to zero aromatic F-T SPKs in the Aircraft Alternative Fuels Emissions eXperiment (AAFEX). This U.S. government funded work was coordinated and run by the U.S. National Aeronautic and Space Administration (NASA). AAFEX test data allowed the authors to study the effect of fuel composition including changes in aromatic content (0 - 18.6% vol) and H/C ratio (1.88 - 2.19) on gaseous and particulate emissions. The authors noted significant changes in particulate emissions as a function of aromatic and sulphur content.

Emissions were measured behind a CFM56-2C1 engine fitted to NASA's a DC-8 aircraft during stationary ground tests at a range of power conditions from idle to maximum thrust. Emissions were also measured from the aircraft's APU across the full range of power and use conditions for JP-8 and one pure F-T fuel provided by SASOL with 0.6 % (vol) aromatic content. The report concludes in general that synthetic fuels had little effect on engine operation or performance whilst providing reductions in engine pollutant emissions. Particulate Matter (PM) mass and number emissions were measured across the full range of power settings for both the APU and CFM56-2C1 RQL combustor. While operating at high power the lowest aromatic content fuel FT-1 produced only slightly fewer particulate mass emissions than slightly higher aromatic content fuel FT-2 (0.6% vol aromatics) and JP-8. As such it would appear that aromatic content should not need to be nil in order to reduce PM emissions considerably for a range of conventional aircraft engines operating at a range of pressure ratios, however it is not possible to determine whether this effect is purely due to reduced aromatics, or also due to other fuel composition changes which are also codependent with fuel processing route such as sulphur content and naphthalene content.

Coincidentally, at low power, Unburned Hydrocarbon (UHC) and Carbon Monoxide (CO) emissions reduced slightly for F-T fuels and their blends. The work of Bulzman et al. was carried out on old combustion technology and such does not include an example of lean burn combustors with complex fuel injector staging systems and combustors which are designed to reduce engine pollutant emissions. As such, these results can only be applied to rich burn systems at this stage.

Kinsey et al. [113] of the U.S. Environmental Protection Agency (EPA) further analyse this particulate matter data gathered at the AAFEX test as shown in figure 5.12. The measured median reduction in PM particle number emissions index for GTL FT-1 and CTL FT-2 fuels was 68.9% and 73.4% respectively. Median changes for GTL FT-1 and CTL FT-2 particle mass emissions index was 94% for both fuels. Notably, PM mass reduces to a much greater extent than PM number. These data are also only valid for conventional rich burn RQL combustors.

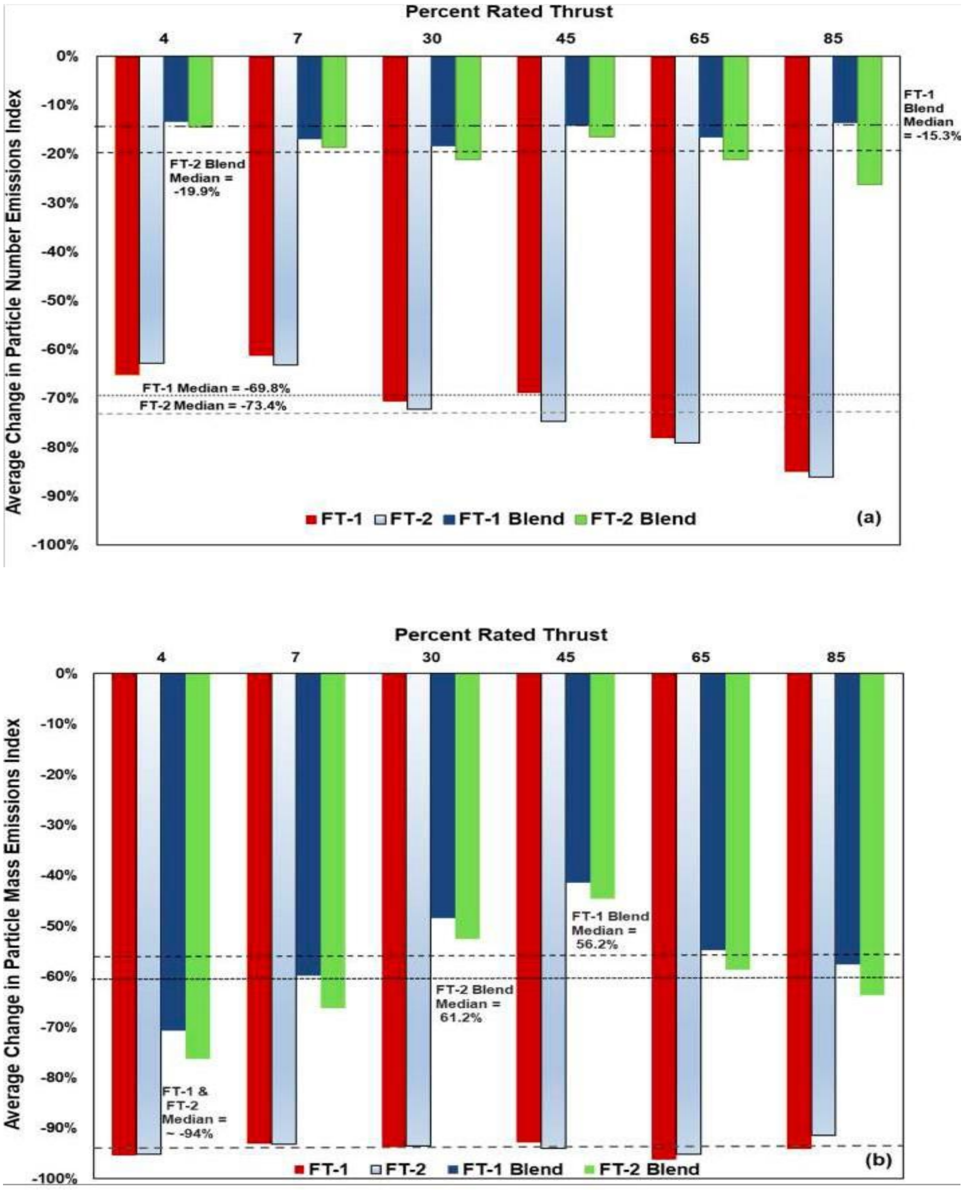


Figure 5.12: AAFEX CFM56-2C1 emissions test. Median change in a) total particle number emissions index, b) total particle mass emissions index from the work of [113]

Impact of fuel properties on aircraft particle emissions

Aircraft gas turbine engines emit CO_2 and non- CO_2 pollutants, including NO_x, CO, HC, and a mixture of PM. In particular, the aircraft PM emissions consist of: (i) soot particles, which include solid particles such as non-volatile particulate matter (nvPM) and metallic compounds; and (ii) volatile PM that arise from fuel sulphur compounds, organic species, and engine lubrication oil [56], [114], [115], [116], [117]. Studies have found that the fuel aromatic and sulphur content primarily influences the aircraft PM mass and number of emission indices (EI), but do not generally impact on gaseous EI such as NO_x, CO, and HC [56], [118], [119], [120].

In addition to the fuel composition, the engine combustor type is also a significant factor impacting the aircraft soot emissions. The current global commercial aviation fleet is predominantly powered by the

Rich-Quench-Lean (RQL) combustor and the lean-burn combustor [121]. Globally, RQL combustors are estimated to power more than 95% of all commercial aircraft in 2019, while lean-burn combustors are increasingly being introduced by newer aircraft types such as the Airbus A320neo, Boeing 737 MAX, and the Boeing 787 families [122]. According to the ICAO emissions database, which is publicly available, RQL engines and lean-burn engines operating in the pilot stage typically exhibit nvPM EI_n that range between 10^{14} and 10^{16} kg^{-1}, while lean-burn engines operating in the main stage have nvPM EI_n ranging between 10^{11} and 10^{13} kg^{-1} [123].

Detailed discussions between the different engine combustor types are beyond the scope of this literature review. Instead, our focus is on reviewing the influence of fuel properties on the aircraft PM emissions, such as the fuel aromatic content (Chapter 2) and its associated engine thrust setting effects, and the fuel sulphur content discussed later in this chapter.

Fuel aromatic content

Results from multiple experimental campaigns, conducted at both ground and cruise conditions and involving different aircraft gas turbine engines, consistently observed a positive correlation between the volume of fuel aromatic content versus the mass and number of the emitted soot particles (Table D.3 and Figure 5.13a). These trends are also observed for other engine types, including different aircraft auxiliary power units [124], [125], [126], turboshaft engines [127], [128], [129], [130], and a compression ignition engine [131].

According to chemical kinetics of the combustion process, the formation of soot in the combustor using a non drop in, aromatics-free fuel takes place in three distinct steps: (i) the fragmentation, propagation, and aromatization of aliphatic compounds to form an initial aromatic ring; and (ii) the creation of additional aromatics rings via the H-abstraction – C_2H_2 (acetylene) addition (HACA) mechanism to form polyaromatic hydrocarbons (PAH), a class of organic compounds comprising of two or more fused aromatic rings; and (iii) the PAHs subsequently nucleate and agglomerate to form soot particles [89], [132], [133]) as mentioned in section 5.1. For fuel containing aromatic compounds, the first step of this process can effectively be circumvented as the aromatics act as additional sites to facilitate the formation of PAHs [134].

In addition to the volume of aromatic compounds in the fuel, laboratory experiments reveal that the type of aromatic species also plays a role in influencing the mass and number of aircraft soot emissions. Saggese et al. [135] observed that polycyclic (multi-ring) aromatics exhibit a higher sooting tendency when compared to monocyclic (single-ring) aromatics. Similarly, Brem et al. [136] found that a 50% increase in naphthalene content, a polycyclic aromatic compound consisting of a fused pair of benzene rings, resulted in a 40% and 30% increase in the soot mass and number emissions, respectively, when the engine is operating at a 30% engine thrust setting. Zheng et al. [131] evaluated 16 different types of aromatics compounds and found that the PM mass and number emissions from fuels with cyclo-aromatics and di-aromatics are around one order of magnitude larger than those with alkyl-benzenes. The differences in soot emissions resulting from different aromatic species are likely caused by variations in the H/C ratio among different aromatic compounds, with polycyclic aromatics exhibiting lower ratios than monocyclic aromatics [131]. For these reasons, instead of the fuel aromatic content, several studies have found that the sooting tendency is better predicted using the fuel: (i) hydrogen mass content and H/C ratio [136], [131] [137], [43], [138]; or (ii) naphthalene content (by volume) [53], [119], [139] because these variables can better capture the chemical differences between mono-aromatics and poly-aromatics.

These findings are reflected in the specification requirements that limit total aromatics to 25% but specifically multi-ring aromatics to 3% (See Chapters 1 and 2).

Engine thrust settings

Data compiled from 13 ground-based experimental campaigns using RQL combustors show that the percentage reduction in soot EI_n varies as a function of the engine thrust settings and changes in the volume of fuel aromatic content (Figure 5.13a). Generally, the percentage reduction in soot EI_n is larger at lower engine thrust settings and becomes smaller at high engine thrust settings [53], [118], [136], [140], [119]. This effect is evident in the compiled ground-based experimental data (Figure 5.14a), where the trendline for data points with thrust settings < 30% (gradient of 4.6) exhibits the steepest decline, followed by data points with thrust settings between 30% and 85% (gradient of 3.8) and data points with thrust settings > 85% (gradient of 2.7).

Brem et al. hypothesised that the engine thrust settings and its associated fuel-to-air ratio is one major factor determining the soot formation pathway in RQL engines [136]. At high engine thrust settings, the RQL combustor operates at a low air-to-fuel (AFR) ratio (rich burn conditions), and under these conditions, the contribution of fuel radicals and products of incomplete combustion becomes the dominant pathway for overall soot emissions. In contrast, during low engine thrust settings, the RQL combustor operates with a higher AFR (lean-burn conditions) which reduces the products of incomplete combustion and causes the dominant pathway for overall soot emissions to shift towards fuel aromatics and PAH formation.

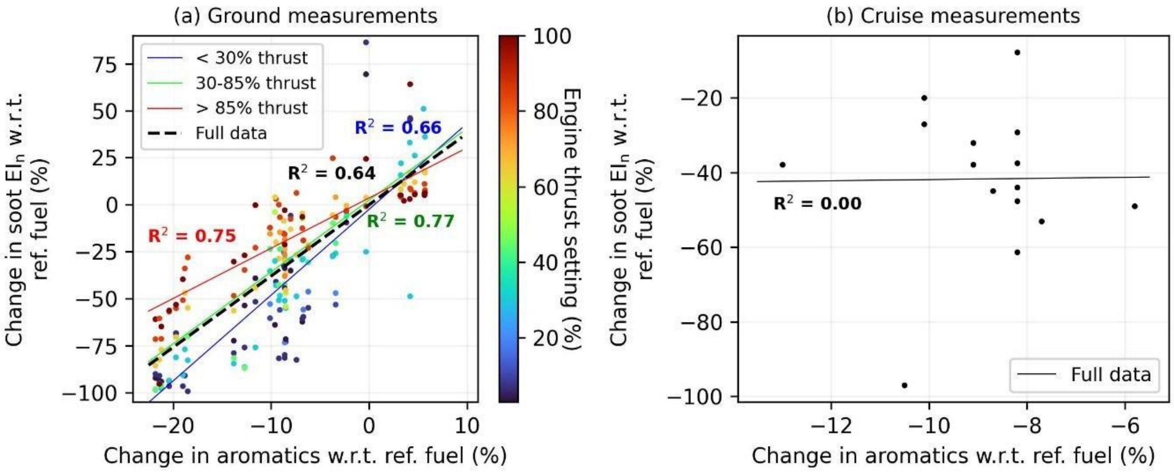


Figure 5.13: Percentage change in the soot EI_n versus the percentage change in the volume of fuel aromatic content relative to the reference (Jet A-1/JP-8) fuel.
The data is compiled from 18 different experimental campaigns at: (a) ground (13 experimental campaigns consisting of 200 data points); and (b) cruise conditions (4 experimental campaigns consisting of 15 data points).

While there are a large number of ground-based experimental campaigns assessing the impact of fuel aromatics on soot emissions, only five campaigns have conducted such measurements at cruise altitudes (Table C.2, presented in Appendix C).

Both ground based and cruise studies shown in Figure 5.13 illustrate a high degree of experimental scatter. Cruise measurements are taken at steady state cruise, high altitude flight conditions so cannot exhibit the full range of power settings.

On average, these five studies found a 40% reduction in the soot EI_n resulting from RQL engines burning different SAF blends that have lower aromatic content than conventional Jet A-1 fuel (Figure 5.13b). This average figure has a large degree of associated uncertainty depending on a degree of factors to be discussed in the following section.

However, unlike results from ground-based campaigns, there is insufficient data to establish a relationship at cruise. (Figure 5.13b). The apparent lack of cause-effect relationship at cruise may be attributed to the increased uncertainty for all cruise measurements relative to ground measurements which are caused by: (i) challenges in measuring the soot emissions from different fuel types under the same operating conditions, because maintaining a constant fuel mass flow rate and engine thrust settings is complicated by variations in the ambient temperature and wind fields; and (ii) additional measurement uncertainties resulting from the variability in plume sampling distance [53] and instrument detection limits [141], [142]. In addition, engines operating at cruise conditions are characterised by higher engine thrust settings that typically range between 40% and 80% [143], causing the dominance of the soot formation pathway to be shifted towards fuel radicals and incomplete combustion products, both of which outweighs the contribution from aromatics and PAHs [136], [119].

For lean-burn engine combustor types, a recent laboratory study that measured the emissions from a concentric lean-burn single-sector combustor showed that: (i) reducing the fuel aromatic content lowered the PM mass and number emissions at both the pilot (rich-burn) and main (lean-burn) stage; and (ii) reductions in the PM mass and number emissions were more apparent at the pilot only splits compared to higher mains to pilot splits, likely because the PM emissions in the pilot stage can be a few orders of magnitude larger than the main stage [120]. However, the impact of engine thrust settings on soot emissions in lean-burn engines remains highly uncertain due to the very limited number of measurements available in the open literature at present.

Complexity introduced by these variables (power setting, altitude, fuel aromatic, free sulphur content etc) result in a high degree of uncertainty in PM emissions, however we can say with a high degree of certainty that, without further detailed analysis:

- Reductions (% nvPMN) in nvPMN emissions at idle conditions due to low aromatics are greater than those at higher power conditions. Baseline conventional fuel PMN emissions are largest at these conditions.
- Reductions (% nvPMN) in nvPMN emissions are lowest at high power conditions, where the conventional fuel PMN emissions are least of all power conditions.
- Emissions at cruise conditions fall within families with all ground conditions at a range of power settings, having a large degree of scatter.
- In all cases, given a large degree of experimental scatter, it can be said that:
    - Zero change in fuel aromatics compositional content produces zero change in nvPM emissions.
    - Reducing the aromatic content of jet fuel increasingly towards zero generates an increasing reduction in nvPMN emissions with a high degree of scatter. There is a strong positive correlation between reducing fuel aromatic content and reducing emissions.
- Generating a numerate trend with uncertainty bands would require further detailed analysis of the available test data.

Fuel sulphur content

Extensive investigations into the impact of fuel sulphur content (FSC) on aircraft PM emissions and its associated contrail formation and properties were conducted through large-scale experimental campaigns during the 1990s, such as SULFUR 1-7 [56], POLINAT [144], NASA SUCCESS [145], and SNIF I-III [146]. Further research efforts have also been carried out in the post- 2000s, including campaigns such as CONCERT [147], [148], NASA APEX, AAFEX and ACCESS [53], [118], [149].

Sulphur emissions from aircraft are directly proportional to the fuel consumption and FSC [150], [151] and are emitted as: (i) gaseous sulphur dioxide (SO_2) which gradually oxidises to form sulphate particles; and (ii) gaseous and liquid sulphuric acid (H_2SO_4) which can either be deposited onto the surface of soot particles, thereby increasing the soot hygroscopicity (i.e., the particle's ability to absorb water from its surroundings), or nucleate to form volatile PM [152], [153], [154]. The conversion efficiency of the fuel sulphur compounds to SO_4 (ε) typically ranges from 0.5% to 10% [56], [155], with a more recent experimental campaigns measuring the gaseous emissions from different modern aircraft types estimating the mean ε to be around 2% [148], [156]. Additionally, ε was also estimated to decrease with increasing EI NO_x, likely resulting from the competition between nitric oxides (NO) and SO_2 for the limited amount of hydroxyl radicals (OH) at the combustor exit [148].

The FSC has a positive association with the number and size of volatile PM and does not appear to impact the number of soot emissions [53], [56], [157]. Specifically, the vPM EIn at cruise conditions: (i) exhibits a weak dependence on aircraft-engine types; (ii) tends to increase from 10^{16} kg^{-1} to 10^{17} kg^{-1} when the FSC exceeds > 100 ppm; and (iii) remains relatively constant at around 10^{16} kg^{-1} at lower FSC levels (< 100 ppm) (Figure 5.15). Observations (ii) and (iii) suggest an increasing contribution of H_2SO_4 to the vPM composition at higher FSC levels, while organic species and lubrication oil droplets may begin to dominate the vPM composition at lower FSC levels. While the vPM EI_n (10^{16} – 10^{17} kg^{-1}) can be up to three orders of magnitude larger than the soot EIn emitted by RQL combustors (10^{14} – 10^{16} kg^{-1}), the vPM particle diameter (< 5 nm) is generally much smaller than that of soot particles (20 – 40 nm) [118]. These differences are likely to result in differences in their activation efficiency in forming contrail ice crystals, as will be discussed in Chapter 6.

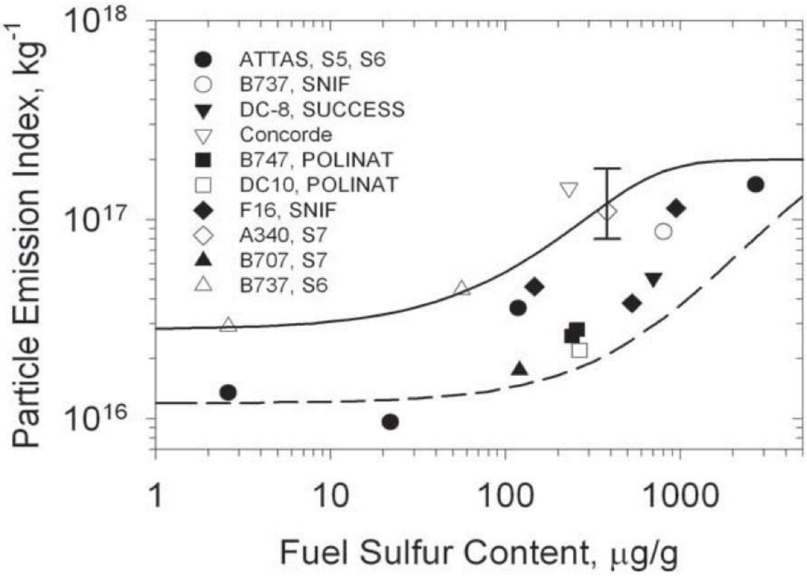


Figure 5.14: The measured particle EI_n (for volatile particles with diameters greater than 5 nm) versus the fuel sulphur content that were compiled from different experimental campaigns. [56]

Linear regression modelling

Moore et al. [53] analyse the effects of jet fuel composition on fuels on Aerosol Emissions from NASAs APEX, AAFEX and ACCESS missions. They compare conventional jet fuels, JP8 and Jet-A with a range of FT (GTL and CTL), and HEFA jet fuels in addition to doping JP-8 with sulphur and use of a high aromatic content Jet A.

Fuels were then tested at sea level static conditions in a CFM56-2-C1 powered Douglas DC-8. Emissions indices (EI) were measured for the full range of fuels and power settings on the same aircraft during the series of tests spanning a total period of a decade. Linear multiple regression modelling was used to determine which fuel and operating parameters had the largest effects on PM EI and equations were developed as a function of operating parameters and fuel composition. Linear regression modelling functions and results from the APEX, AAFEX and ACCESS tests can be seen in Figure 5.15 from [53]. These plots show the measured emissions index for 9 different indices against a linear regression model output for available test data. Data in the blue histogram illustrates the frequency of certain air fuel mixtures taken into account in the development of the linear regression model. Equation callouts within each graph show the logarithmic linear regression model and its constants for the emissions index of interest.

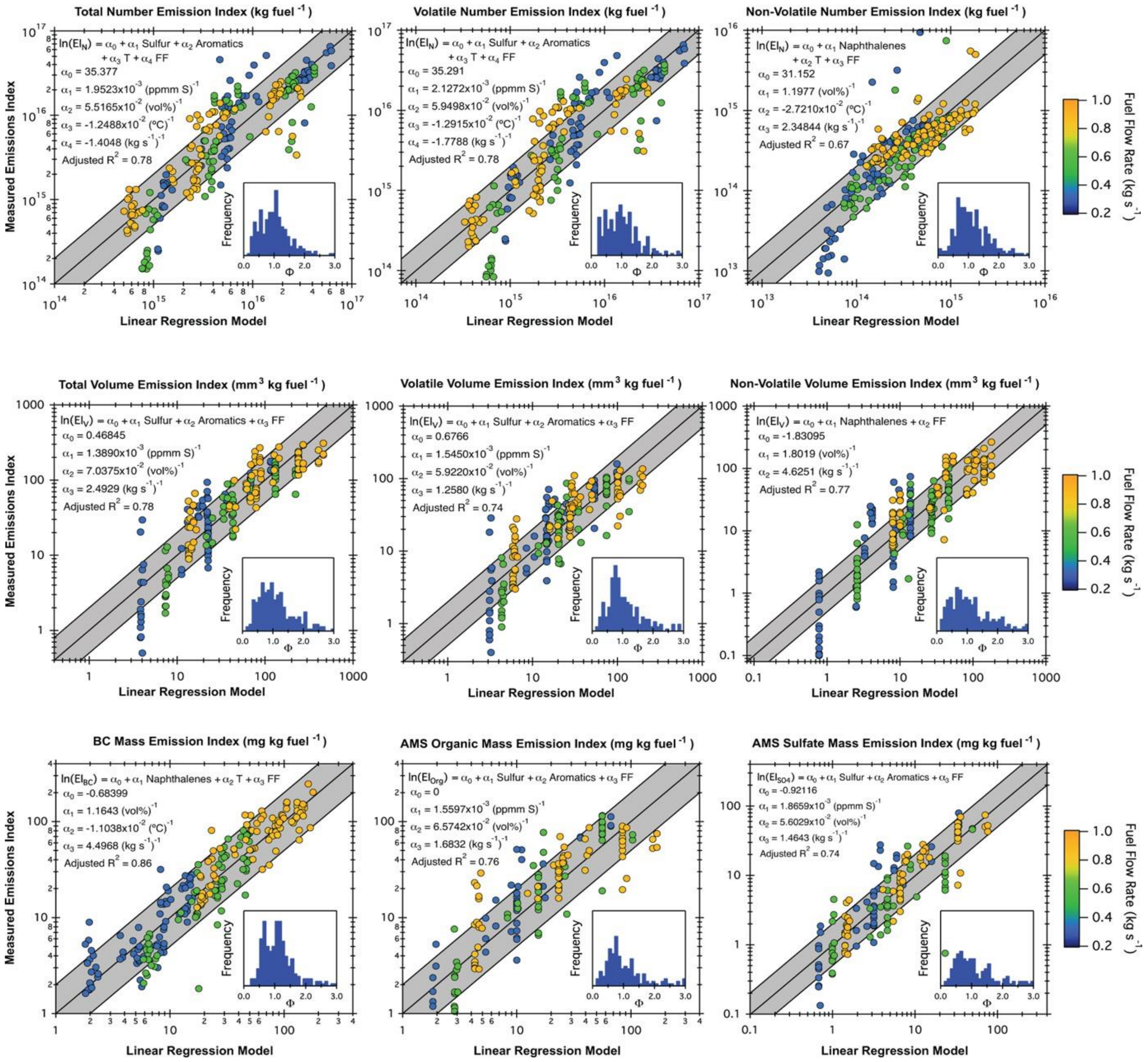


Figure 5.15: Results of linear multiple regression modelling applied to NASAs APEX, AAFEX and ACCESS missions form the work of Moore et al. [53]

The authors reach key conclusions on PM emissions for an RQL combustor which each depend on the following factors in addition to sample temperature and engine fuel flow:

- Total PM number EI and Total PM volume EI is a function of fuel sulphur content and aromatic content.
- Black Carbon Mass EI was seen to be a function of fuel naphthalene content.
- AMS organic carbon EI and AMS sulphate mass were both seen to be a function of sulphur and aromatics.

Clearly, fuel aromatic content is a key fuel parameter, however sulphur content also has a large influence on PM number and volume EIs. PM Mass EIs showed strong correlations with di- aromatic content as did Non-volatile volume and number EIs. Consequently, a fuel with a low di-aromatic content, aromatic content and sulphur content is expected to produce a lower nvPM emissions.

Further to the work cited in tables D.2 and D.3 it is possible to re-plot the data to determine nvPM emission index trends against change in fuel composition as seen in figure 5.16 for total aromatics content, 5.17 for naphthalene content, 5.18 mono aromatic content and 5.19 hydrogen content. Each of these additional plots show experimental uncertainty analysis based on the values quoted in the original literature. Each plot shows a mean (dotted) line thought the data set and zero at the axis intercept. +/- 1 standard deviation is plotted onto the data set either side of the mean (solid lines)

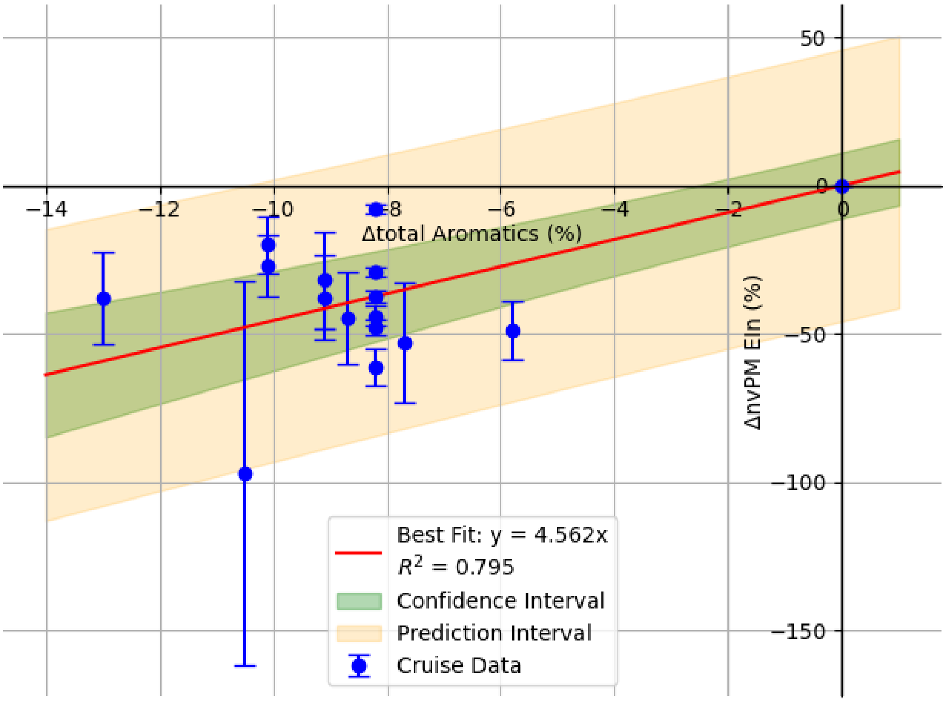


Figure 5.16: Percentage change in the cruise nvPM EIn versus the percentage change in the volume of fuel total aromatic content relative to the reference (Jet A-1/JP-8) fuel

The data is compiled from 4 campaigns at cruise conditions (4 experimental campaigns consisting of 15 data points)

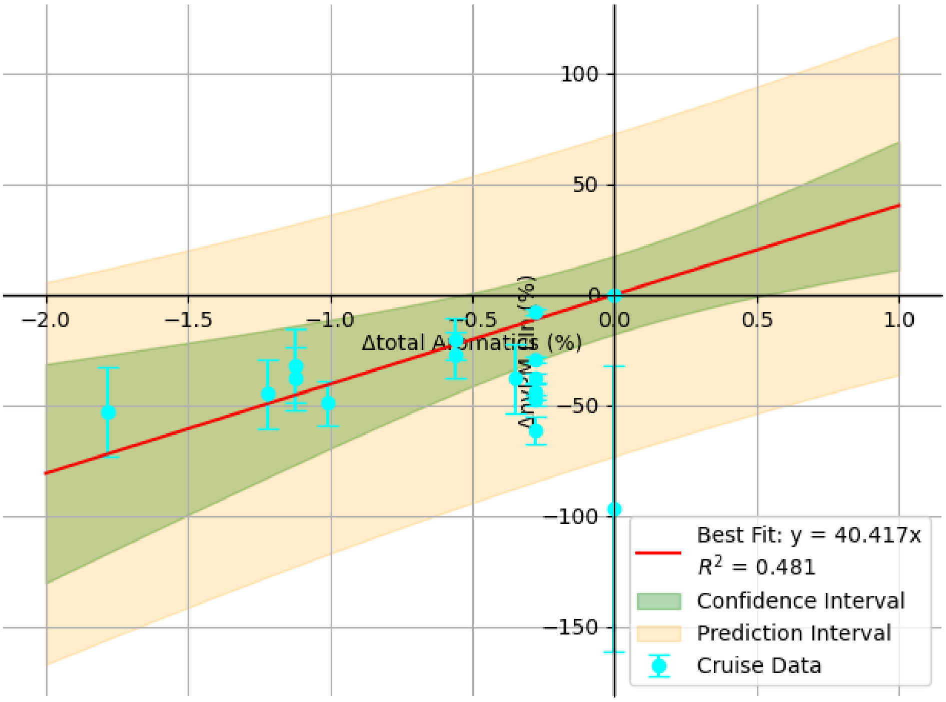


Figure 5.17 Percentage change in the cruise nvPM EIn versus the percentage change in the volume of fuel total naphthalene content relative to the reference (Jet A-1/JP-8) fuel

The data is compiled from 4 campaigns at cruise conditions (4 experimental campaigns consisting of 15 data points)

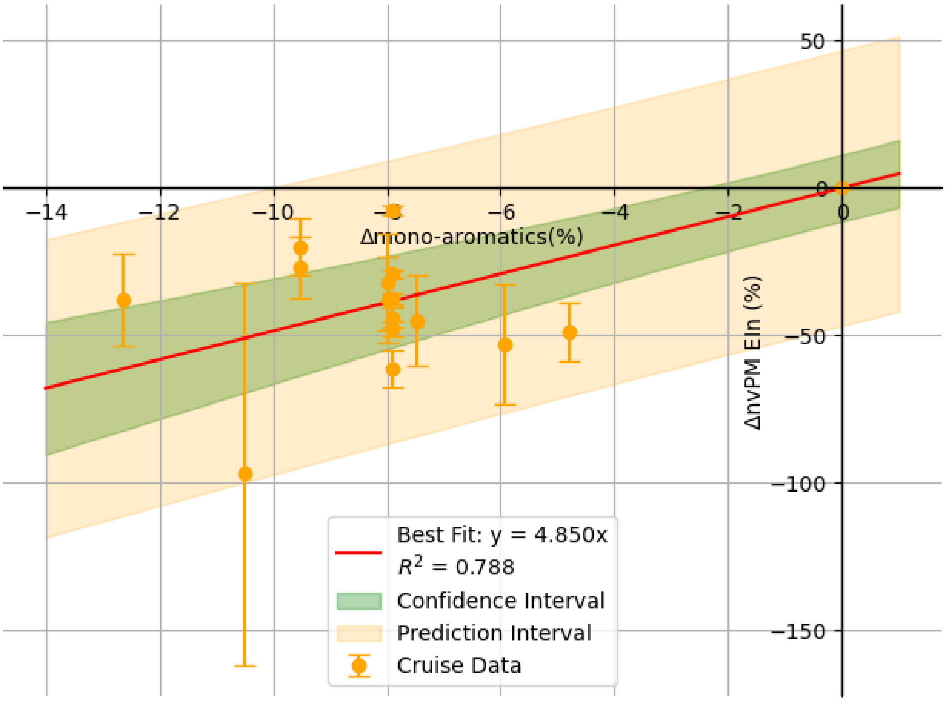


Figure 5.18 Percentage change in the cruise nvPM EIn versus the percentage change in the volume of fuel total mono-aromatic content relative to the reference (Jet A-1/JP-8) fuel

The data is compiled from 4 campaigns at cruise conditions (4 experimental campaigns consisting of 15 data points)

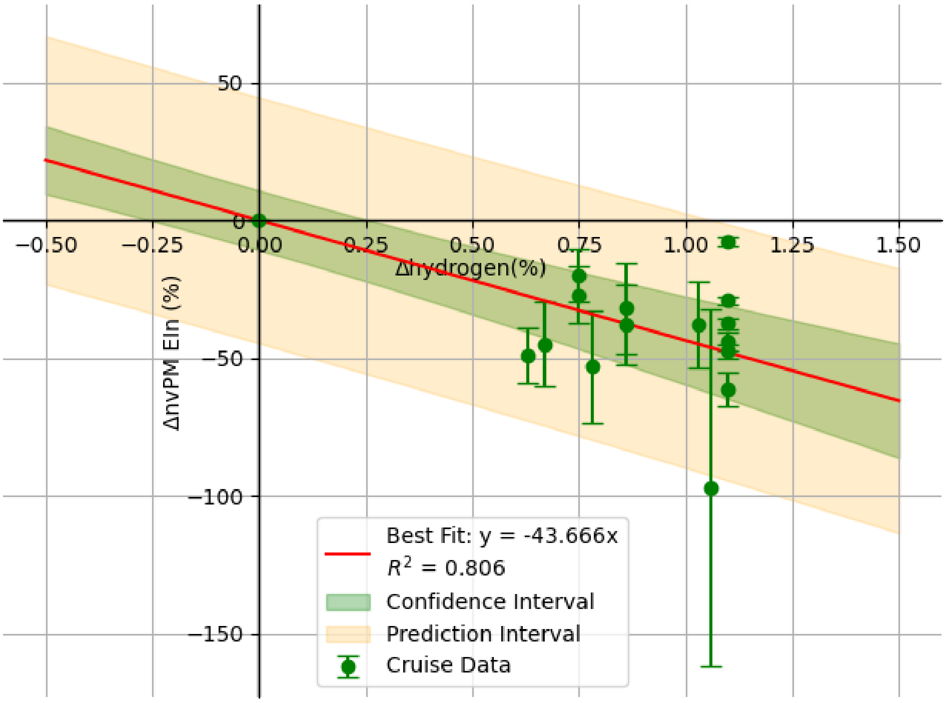


Figure 5.19 Percentage change in the cruise nvPM EIn versus the percentage change in the volume of fuel total hydrogen content relative to the reference (Jet A-1/JP-8) fuel.

The data is compiled from 4 campaigns at cruise conditions (4 experimental campaigns consisting of 15 data points)

The data clearly indicate a high degree of experimental scatter for nvPM emissions taken at cruise, resulting in low confidence in the conclusions drawn, however based on these figures it can be said that:

- nvPM emissions are likely to reduce with reduction in total aromatic content, mono- aromatic content and naphthalene content.
- Naphthalene content reduction has a stronger effect nvPM reduction than mono- aromatics or total aromatics like for like (per vol%)
- There is a high degree of experimental scatter in each plot, likely due to changes in thrust setting, engine hardware, aircraft engine loading, engine pressure ratios and combustion process residence times.
- This data agrees with the summary presented from the linear regression model work presented above and previous statements made about more complex aromatic structures generating higher nvPM emissions.

Additionally, Zheng et al. [131] study the effect of aromatic type and structure on PM emissions generation from a low TRL rig run at near atmospheric conditions. Their experiments find that alkyl benzenes, in general, generate lower PM mass concentrations than cyclo-aromatics, and cyclo-aromatics and alkyl-benzenes both produce less PM mass emissions than di-aromatic structures. Essentially, higher orders of aromatic structural complexity result in greater PM mass emissions when reacted with air at atmospheric conditions.

Lieuwen and Yang [104] state in their work on gas turbine emissions that conventional RQL aero combustors are likely less sensitive to fuel composition as the emissions reducing portion of the combustor (dilution zone) is downstream of the fuel injection and primary zone of the combustor, which is more sensitive to fuel atomization and spray cone angle. As such Lieuwen et al. propose, based on the work of Brown et al. [158] state that modern lean combustion systems which rely much more heavily on carefully controlled aerodynamics, atomization and fuel placement are likely to prove more challenging for control of emissions. The validity of this hypothesis will be dependent on atomiser, combustor and control system dependant and warrants further investigation. It is possible that this could be mitigated using atomisers which use prompt mode atomization (liquid jet in high velocity cross flow) as this is less sensitive to fuel composition as stated by Lefebvre et al. [105].

Table 5.3 Considerations to quantify before using low aromatic content fuels in rich burn systems

Potential Benefits	1. RQL combustor PM emissions exhibit a high degree of sensitivity to aromatic content, showing ~70% and 94% median reduction in PM number and mass emission respectively throughout a CFM65-2-C1 turbofan thrust range using conventional combustor technology. 2. RQL combustors show percentage reduction in soot EIn is larger at lower engine thrust settings and becomes smaller at high engine thrust settings This effect is evident in the compiled ground-based experimental data where the trendline for data points with thrust settings < 30% (gradient of 4.6) exhibits the steepest decline, followed by data points with thrust settings between 30% and 85% (gradient of 3.8) and data points with thrust settings > 85% (gradient of 2.7). 3. **Cruise PM emissions** could be reduced by 40% or more, however the data are sparse and show high experimental uncertainty. 4. **PM emissions can be reduced by the reduction of sulphur and naphthalene content** as well as aromatic content, all of which are reduced by hydro-processing of jet-fuels. 5. As well as the overall level of aromatics, the classes of aromatic compounds present have a direct effect on PM emissions. **Aromatic species exhibiting higher HD produce greater PM emissions.** PM EIm and PM Ein were seen to increase by an order of magnitude at lab scale when changing the aromatic species from mono-aromatic structures to di-aromatic structures. 6. **Reduction of sulphur content** in jet fuels from 1000 – 1 µg/g has the potential to reduce PM EIn by an order of magnitude. This reduction will depend on other components in the fuel , as well as sulphur alone. 7. **Combustor liner life** will likely increase with lower aromatic content and higher hydrogen content (lower flame radiative thermal emission), reducing the cost of engine service and overhaul for operators.
Potential Risks	8. **Changes in ignition stability** due to Cetane Number changes may affect the combustion system high altitude relight envelope. this warrants further testing at high TRL, drawing from the conclusions of previous work

Lean burn combustion system PM emissions

The purpose of this section is to understand the effect of fuel chemistry changes on current lean burn combustion system hardware, which at present represents a smaller portion of the civil aviation fleet than RQL combustion systems. An overview of lean burn combustor technology is provided in Appendix C.

Hicks et al [102] studied the effect of burning JP8 and a Hydrotreated Renewable Jet [HRJ] fuel derived from beef tallow in using a GE TAPS lean premixed prevaporised (LPP) atomiser. Blends of both fuels were tested. They state that 50/50 blends of the fuels provide no benefit in terms of fuel cost or performance. As such they ran 100% JP-8, 25% HRJ / 75% JP-8, 75% HRJ / 25% JP-8 and 100% HRJ fuels. Standard fuel tests were run on the HRJ, finding that the fuel contained < 3 ppm of sulphur, 0.4% (vol) olefins, 0.4% (vol) aromatics and 0 % (vol) naphthalenes. HRJ fuel exhibited initial boiling point was higher than that of the JP-8, and the final boiling point was lower than that of JP-8 on test. The Cetane index of the HRJ fuel was 67 compared with 41 for the JP-8. Viscosity and hydrogen content of the HRJ were also higher than that of JP-8. These figures and trends are in keeping with F-T processed low aromatic content fuels.

Combustion tests were run on a research TAPS injector and the combustion research facility at NASA Glenn Research Centre, Ohio, using a test rig hardware and optical measurements described in earlier work of Hicks' et al [159]. This test facility is equipped to measure the full suite of gaseous emissions while simultaneously measuring laser scatter from fuel droplets, CH* and OH* radicals which represent carbon/PM matter and the flame front respectively with high-speed optical measurement equipment. As a result, it is possible to quantify fuel spray cone angles, fuel atomisation and evaporation as well as the location of heat release and changes with respect to fuel. All of this can be done while measuring gaseous emissions.

Hicks et al [102] found no significant change in the gaseous emissions (NO_x, CO and UHC), however there were notable changes in the OH chemiluminescence images due to altered fuel chemistry. Notably, the shape of the pilot flame is altered with increasing HRJ fuel %. Specifically, HRJ fuel tends to generate less chemiluminescence (CH*) as a result of fewer soot particles being generated by the HRJ, additionally. This is more evident when running with high 20%/80% pilot/main fuel split, which shows a considerable reduction in CH* when switching from JP-8 to a 25% JP-8 – 75% HRJ fuel mix. At the pilot only condition, which would represent an aircraft approach fight phase according to this work, the total CH* signal reduces ~ 25%. This cannot be directly correlated with PM readings but is an indicator of the presence of particulates. The work also notes that HRJ fuels appear to react much more readily at high power conditions with both mains and pilot fuel circuits flowing than JP-8. This paper concludes that there are changes in fuel placement, spray cone angle, PM emissions and combustion flow field with a change in fuel.

Flames and sound waves can couple in combustors generating a feedback loop called combustion thermo-acoustics, also known as rumble. The flame's location in the combustor depends on fuel placement and combustion gas aerodynamics which control the shape of the flow-field. The flow-field is also dependent on flame location and subsequent density changes, which generate sound. As a result, changes in spray cone angles, fuel placement and combustion flow field due to changes in fuel composition will likely change combustor rumble. The change in flow field would likely cause changes to the pattern factor the inlet to the turbine inlet guide vanes, impacting component life. Furthermore, it is possible that this change in heat release location will affect the radiative and convective heat flux reaching the fuel atomiser and change the wetted wall temperatures (WWT) of the fuel circuit, altering injector in service life.

Okai et al [120] also test the effect of changing fuel in a lean burn research combustor at high pressure and high temperature using Japan's JAXA AP7 combustion test rig. The fuel injector contains two separate fuel circuits, a main (lean) and pilot (rich) circuit each with a concentric pre-filming annular fuel atomiser lip. The work of Okai et al also shows a pilot cup and six concentric air swirlers used to control the swirling, recirculating flow field downstream of the injector.

Test conditions (shown in top left plot of Figure 5.20) range from pilot only engine idle conditions at inlet temperatures of 250°C and 5.5 bar to 564°C and 20 bar with pilot and main fuel circuits flowing at a simulated maximum take-off condition or 530°C at 30 bar simulating a pilot and main climb condition.

The injector used for this testing includes a cross flow refilming pre-vaporised main fuel atomiser and a separate pre-filming air blast pilot fuel atomiser [120].

The authors took images of the flame and compared them with gaseous and PM emissions (mass and number) finding that the main change in PM emissions is generated when any rich burn pilot flame is in operation. A suite of emissions data (CO, THC, NO_x, PM number and PM mass) is reproduced from the work of Okai et al. [120] in Figure 5.20.

The pilot/mains split is not published for conditions other than pilot only. However in the idle and approach cases the use of HEFA in comparison with conventionally sourced Kerosene reduces PM number emissions by approximately 50% and PM mass emissions by approximately 90% . This suggests that HEFA emissions are half as frequent (PM number) and five times less in mean volume in this case. It is noteworthy that there are some PM Number emissions with low corresponding PM mass emissions at the richest cruise conditions at 20 bar climb and 20 bar max take off conditions when testing with conventional jet fuel. All of these emissions were reduced to near zero when the fuel was switched to HEFA. These high PM emission lean burning conditions presumably generate higher emissions due to richer pilot operation at richer rig AFRs.

Furthermore, it should be noted that low power operation of the test rig close to idle conditions with HEFA produced a blue flame whether testing pilot only or 20/80 pilot main split. When the same condition was tested with conventional jet fuel containing a higher proportion of aromatics (~19%) the pilot only case clearly generated a yellow flame, indicating a higher carbon content of the flame. This change was less obvious visually with a 20% pilot split.

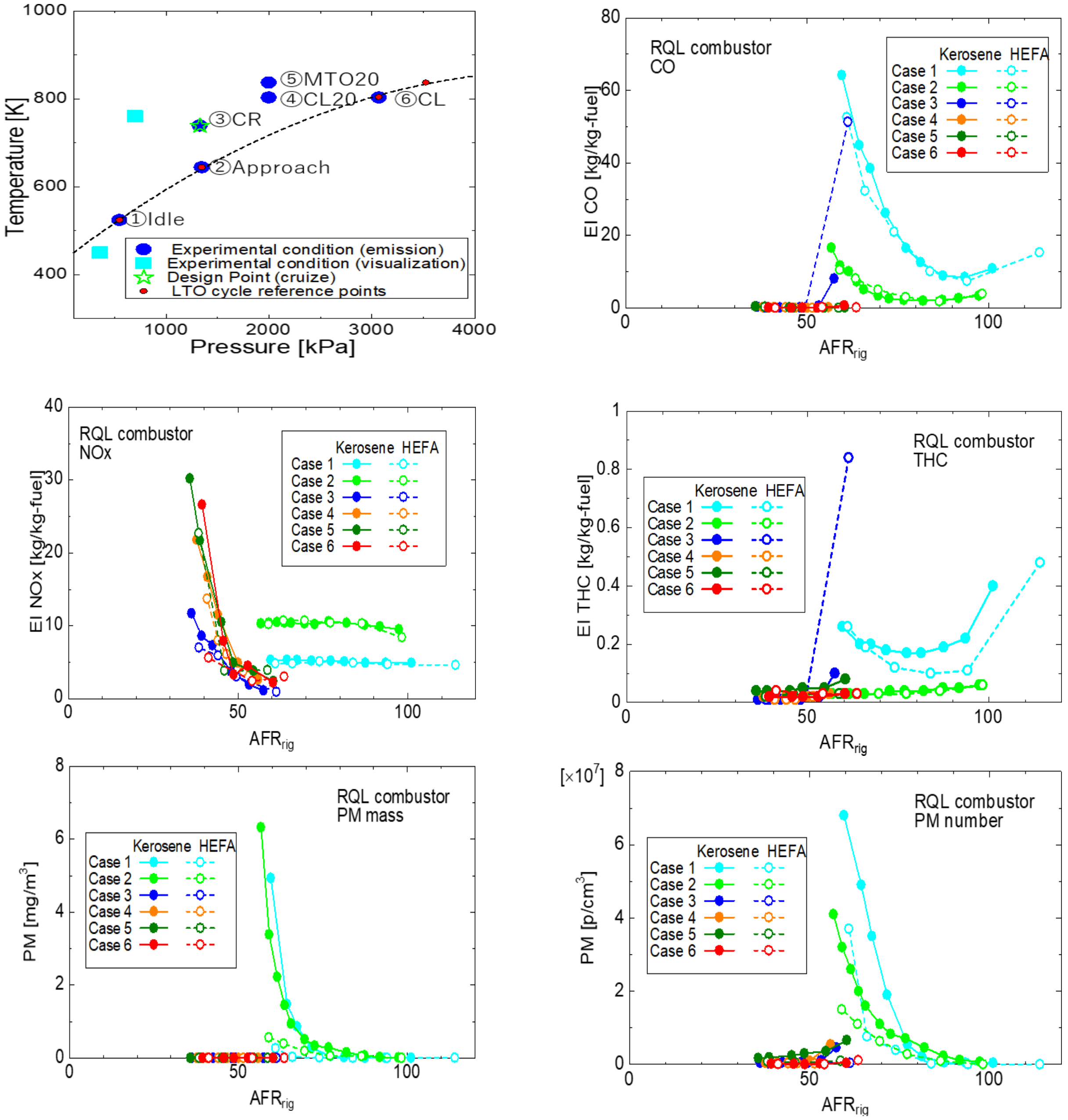


Figure 5.20: Lean burn combustor emissions from the work of Okai et al. [120]. Testing carried out at JAXAs AP7 combustion test rig with six concentric air swirlers and two (pilot and main) air blast atomisers

Figures appear to be incorrectly labelled RQL combustor, as the injector is a lean burn concentric twin fuel circuit DI, piloted LPP main lean burn injector, additionally cruise is misspelt as cruize

Sub figures: Upper left operating condition reference. Upper right CO emissions; Mid left, combined NO_x emissions, mid right Total Hydrocarbon (THC) emissions. Lower left PM mass, Lower right PM number

Table 5.4 Considerations to Quantify Before Using Low Aromatic Content Fuels in Lean Burn Systems

Potential Benefits	1. **Lower pilot only PM emissions** (mass and number) when running the engine at ground idle and approach conditions when the pilot split to main is higher. 2. **Lower PM emissions when running high power**, rich conditions, particularly with a higher pilot split.
Potential Risks	1. **Rumble:** Change in combustion aerodynamic flow fuels due to differing heat release which could in turn change the combustor thermo-acoustic tones and possibly change the combustor's rumble response. This could potentially lead to structural failure in the combustor due to thermoacoustic resonance if fuel changes are not understood, characterised. and tested at the engine certification stage. Cetane number (as a burning quality index) can be used to determine what is normal for current conventional fuels in comparison with alternative or highly hydro-processed fuels. 2. **Liner and fuel spray nozzle service life reduction**: Change in location of heat release, with low aromatic fuels typically igniting further upstream then conventional jet fuel as a comparatively greater proportion of smaller diameter droplets within the spray and a higher fuel cetane number (reduced ignition delay time) result in reactions closer to the combustor dome. This could potentially change the combustor liner, heat shield tile and injector life. There may also be implications for fuel coking depending on the radiative and convective heat flux into the fuel injector which will alter the fuel circuit wetted wall temperature (WWT) and potentially accelerate coking, particularly where there is a blend of conventional Jet fuel and low aromatic content fuel, since conventional jet fuel is more prone to coking and low aromatic fuels are likely to generate higher fuel injector WWTs. 3. **Turbine inlet guide vane (IGV) life reduction**. Pattern factor change due to altered spray patternation, fuel ignition delay and change in flow field in lean burn combustors.

5.8. Discussion

According to ground-level static measurements, between 8 and 0% aromatics there is a significant reduction in nvPM emissions, which is a non-linear process with aromatic content. This is not borne out by the available data from flight tests at cruise conditions but may be due to the lack of data availability. Additionally, by reducing aromatic content to zero, engine CO_2 emissions will be theoretically reduced by 3% relative to conventional jet fuels as the energy content per unit mass increases. An overview of the impacts of increased hydrotreatment on conventional fuels is shown in Figure 5.21 overleaf.

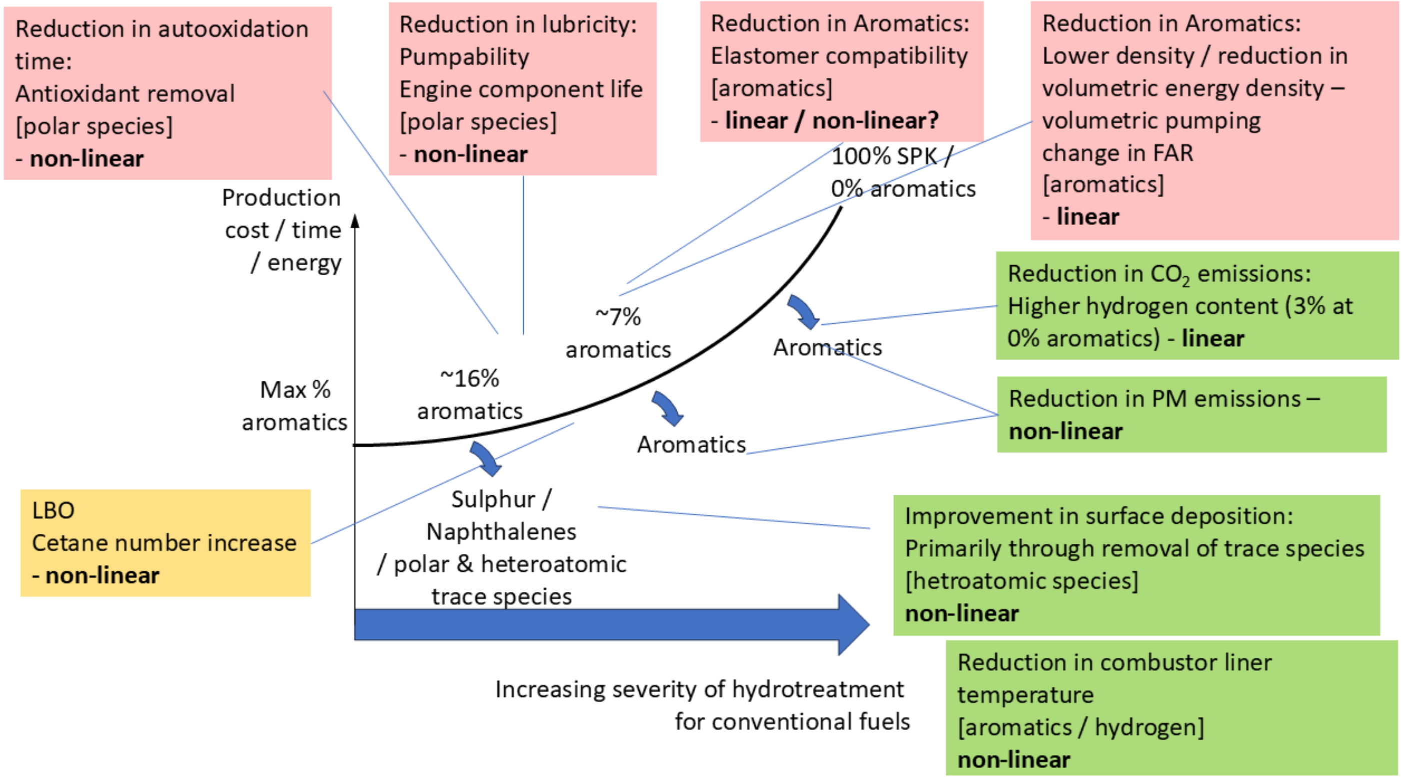


Figure 5.21: Overview of the impact of increasing hydrotreatment on fuel system and combustor performance

5.9. Research gaps

Future research should consider carefully how low aromatic content fuels are measured in situ during low TRL atomisation and combustion tests when comparing with a higher aromatic content fuel. This is because laser spectroscopic techniques used for regular jet fuels containing large fractions of aromatics do not work well for low aromatic content fuels.

i. The fundamental understanding of smoke production from branched alkanes (is- paraffins). Global based correlations such as HD and type of aromatic content provide a useful but limited insight into the sooting tendency of jet fuel. However, these global corrections are not sufficient on their own to fully describe this complex phenomenon.

   To investigate the relationship between chemical composition such as highly branched alkanes, the sooting propensity should be investigated. It is important to investigate the complex interplay between jet fuel composition especially different types of aromatics and engine cycle on aviation particle emissions. In particular, the evolution of change in soot production as the HD (or other metrics) reduces. It is likely that any change to the specification of fuels should take small reduction steps, similar to the ULSD change which took over 15 years (and would be required for the industry to accept / adapt). Understanding the change in soot production as that change is implemented in steps would be valuable.

   Removing naphthalenes (only 3% by volume) would represent a non linear reduction in soot. A choice of metric needs to be made to assess linearity - HD useful, however it is calculated not measured. The optimal would be an HD of 0, but this would be challenging for a number of reasons, principally it is almost impossible to measure in a specification test.

This approach may enable to also provide recommendations for ideal jet fuel composition to minimise non-CO_2 emissions accelerating mitigate of aviation emissions.

ii. Parametric testing of the same base fuel but with varying aromatics due to severity of hydrotreatment. This should be carried out across the full range of parameters of interest (for example, flashback, atomization, high altitude relight) and TRLs.

iii. Severe hydrotreating of fuels is likely to increase the cyclo-aromatic content of fuels with the current industry limit around 30-50% max, however there is no good data to provide rational limits on this quantity. This warrants further testing across the range of combustor operability parameters.

iv. Simplification of combustors may be possible as a route to generating further improvements in emissions over time – this would require further research to quantify design rules and study emissions effects as well as operability limits.

Further detailed research into prefilming air blast atomiser droplet size changes in isolation to combustors for a range of fuels at realistic test conditions may reveal useful information to inform design choices for combustors or assess the risk of changing fuel composition. Currently, the available research would suggest no change in droplet diameter with fuel choice. Ignition stability at low pressure for the range of fuels considered using a full screening test at Low TRL and representative pressure and temperature.

v. Liner and injector life: Change in location of heat release, with low aromatic fuels typically igniting further upstream then conventional jet fuel as a comparatively greater proportion of smaller diameter droplets within the spray and a higher fuel cetane number (reduced ignition delay time) result in reactions closer to the combustor dome. This could potentially change the combustor liner, heat shield tile and injector life. There may also be implications for fuel coking depending on the radiative and convective heat flux into the fuel injector which will alter the fuel circuit wetted wall temperature (WWT) and potentially accelerate coking, particularly where there is a blend of conventional Jet fuel and low aromatic content fuel, since conventional jet fuel is more prone to coking and low aromatic fuels are likely to generate higher fuel injector WWTs. This effect is likely to be different for lean burn combustors, which are shown to be sensitive to changes in fuel aromatic content.

vi. Turbine inlet guide vane life. Pattern factor change due to altered spray patternation, fuel ignition delay and change in flow field in lean burn combustors.

vii. Back to back testing of lean burn and RQL combustors while changing fuels at low TRL taking the full suite of PM emissions, droplet evaporation measurements, CH* chemiluminescence and fuel PLIF would allow conclusive statements to be made about how conventional fuels and alternative, heavily hydrotreated fuels react in the in service fleet or aircraft, and how they may react in the future with a higher portion of in lean burn combustors in service. This work should ideally include tests for a variety of injector types to allow conclusions to be made regarding pressure swirl atomisers, comparing with LDI prefilming air blast atomisers, LPP cross flow atomisers. Key questions this work would aim to answer are:

a. How does fuel composition affect heat release through differing atomization, droplet formation, break up, evaporation and heat release in different combustors using different emissions reduction technologies. (RQL, Lean burn LPP and Lean burn LDI)
b. How does fuel composition change chemical kinetic and fuel spray as well as droplet evaporation in realistic single sector combustor low-mid TRL environments.
c. How would this change in fuel chemistry affect heat release in the combustor and hence the thermal environment? How would changes in fuel chemistry change liner and fuel spray nozzle temperatures in either technology. What effect would this have on component life. Could more heat be transferred to the fuel as a result.
d. What are the potential risks and benefits of changing fuel composition on different flight phases in aero engines with different fuel atomisers. Are some atomisers more suitable for use with alternative fuels than others.

Flashback presents a risk wherever LPP injectors are used, for example in some modern lean burn LPP injectors which are installed and in use on <5% of current civil aviation flights.

viii. The effect of fuel composition on flashback in realistic fuel atomisers and combustors has not been studied in great depth within the open literature. Design of a test rig to measure this flashback, as a matter of safety, in the range of lean burn atomisers would be highly valuable and arguably essential prior to addition of a higher cetane number fuel to the fleet of Inservice aircraft fitted with a range of combustor and atomiser technologies.

ix. Further research should be carried out, if not already completed, by OEMs across the range of TRL levels to ensure safe, reliable and cost-effective flight for passengers and operators.

x. The impact of thrust settings in lean-burn engines on soot emissions remains highly uncertain as there are very limited measurements available in the open literature at present. This warrants further research.

Closing the gap **test campaign**

The comprehensive literature review has highlighted gaps in our understanding of fuel chemical composition’s impact on soot and ice crystal formation. Closing these knowledge gaps are crucial for addressing non-CO_2 emissions and understanding how jet fuel composition, such as types of aromatics influences soot particle formation. To embrace closing this gap a primary research test campaign was undertaken to provide in-depth information in all relevant dimensions: Five types of fuel were selected considering an envelope of variations in their aromatic component. The fuels were designed and blended to investigate the effects of aromatics on soot particle emissions. The sulphur content of the hydrotreated jet fuels was kept low to explore the influence of the changing hydrogen content while controlling for the sulphur effects on soot particle activation and volatile particle formation. The result from these tests paves the way to close the knowledge gap relating to soot-forming tendencies of jet fuels allowing for guidelines for fuel specification with the objective to significantly reduce the climate impacts of aviation fuels. During the test campaign in addition to measuring particle emissions (mass and number) of a large variety of jet fuels with wide range of aromatics % (hence different H/C ratio and %H), the other properties such as density, viscosity, and auto-ignition-temperature, which are important from an engine and aircraft compatibility and operability standpoint was investigated.

Reduction in aromatic content of Jet A-1 fuel has multiple advantages from the emission reduction point of view. The *Closing the Gap* jet fuel test campaign confirms:

- nvPM emission characteristics, including particle number, particle mass, and particle size distribution produced from APU ground test, are analysed and compared for Jet fuels with different aromatic content. The results indicate that jet fuels with lower aromatic content reduce particulate emission and generate smaller size nvPM.
    - Jet A-1 fuel with 13.1% aromatics showed 19% reduction (in mass) and Jet A-1 fuel with 7.1% aromatics achieved a 58% reduction (in mass) compared to conventional Jet A-1 with 14.5% aromatics (at full load condition).
    - Jet A-1 fuel with 13.1% aromatics showed 12% reduction (in particle number) and Jet A-1 fuel with 7.1% aromatics achieved a 33% reduction (in particle number) compared to conventional Jet A-1 with 14.5% aromatics (at full load condition).
    - The reduction in nvPM is the most significant at low APU engine power settings.
    - Detailed analysis of fuel composition using GC-GC indicates that Naphthene has the leading order impact on particle formation. Jet A-1 fuel with reduced naphthalene showed greatest tendency towards lowering nvPM emissions.

- There was no significant change in NOx emissions based on the aromatic content of the fuel. However, the NOx Emission Factor (EFNOx) decreased by 2.5% when Jet A-1 fuels reduced their aromatic content from 14.5% to 7.1%.

- Experimental results confirmed fuel consumption (by mass) reduced as the concentration of aromatics (hence increase in H/C ratio) in jet fuels reduced. Jet A-1 fuel with 13.1% aromatics demonstrated a 0.5% decrease in fuel consumption and Jet A-1 fuel with 7.1% aromatics demonstrated a more significant 1.8% reduction in fuel consumption compared to conventional Jet A-1 with 14.5% aromatics.

Appendix D provides further information on the primary research test campaign, experimental setup, deliverables and results.

5.10. Conclusions

Engine hardware is insensitive to the source or refinery processing, providing the fuel chemistry is consistent at the point of delivery to the combustor. As such, the conclusions listed below also hold for synthetic kerosenes containing synthesised aromatics providing the aromatics are well distributed across the boiling range. Control of aromatic content by ASTM D1319 appears to be adequate for the final fuel, although there may be limitations required on cyclo-aromatics, i.e., tetralins and indans, to assure the synthesised product has a composition that is typical of experience with conventional jet fuel [40]. [Note, confidence statements below are preliminary and are subject to further discussion and feedback]

1. In the absence of parametric testing on conventional fuels data /information from SPK studies has been used as this is a useful indication of impact of changes in aromatic content in conventional fuels. **(medium confidence)**

2. Increasing fuel H/C (lower HD) results in reduced combustor liner temperatures and increased combustor liner life. **(high confidence)**.

3. Low aromatic content GTL fuels will result in marginally smaller mean fuel droplet sizes as a result of changes in viscosity and fuel boiling point. However the literature for fuel sprays (in Figure 0.9) also suggests that low aromatic content fuels produce a larger portion of smaller droplets in pressure swirl atomisers, which suggests a change in the physical process of droplet breakup. Further research on droplet distributions in different injectors and operating conditions is required to determine whether this effect is present in all other injector types. **(low confidence)**

4. Tests were carried out to determine the lower flammability limit of conventionally sourced Jet-A and synthetic, FT-IPK. Results show that FT-IPK is able to ignite at lower fuel air ratios (mass ratio) than Jet-A. **(high confidence)**

5. Lower aromatic content in fuels will result in shorter ignition delays due to higher cetane number than conventional Jet-A. **(high confidence)**

6. Lower aromatic fuels will have a reduced fuel air ratio (mass %) at the lower flammability limit when compared with Jet A-1. **(high confidence)**

7. Reduced fuel aromatic content may alter flashback performance in LPP injectors and may pose a risk to safe operation of aircraft without adequate changes being made to the fuel staging strategy onboard aircraft. **(medium confidence)**

8. Differing heat release and droplet evaporation curves during combustion.
    a. If FT-FSJF droplets are smaller, and the flame is taking longer to burn this suggests that either the droplet evaporation rate is lower or ignition is taking place at an earlier point in the spray, closer to the injector. This would then release heat closer to the combustor dome, evaporating fuel faster than in the case of Jet A-1, on average. It could be postulated that this is due to a change in fuel cut and higher proportion of readily available fuel, resulting in a change in droplet break up behaviour due to surface tension coupled with shorter ignition delay resulting in greater heat release close to the injector or combustor dome reference point. This warrants further, integrated study with appropriate measurement techniques, preferably in a collaborative manner to achieve satisfactory conclusions. **(low confidence)**

    b. Lower aromatics will result in longer droplet evaporation time at low power (presumably due to fuel evaporation changes rather than droplet size). **(medium confidence)**

    c. Reduction in the extremities of the ignition loop (light up/ lean blow out) at high altitude conditions (over 32 kft at high Mach numbers) on full annular combustors. High Altitude tests carried out using the R-R Derby SARS rig do not confirm this result- perhaps because the conditions were not as extreme. Further work is required to study these effects and discuss findings in the open literature before being able to reach a high degree of confidence regarding combustor ignition loop operability with FT-IPK fuels. **(medium confidence, differing results at TRL 3 to~TRL 5)**

nvPM emissions:

9. Laboratory results reveal that the species of aromatic plays a role in determining the mass and number of aircraft soot emissions. Mono-cyclic aromatics have a lower sooting propensity than multi-ring aromatics. These findings are reflected in the current specification that limits total aromatics to 25% but multi-ring aromatics to 3%. **(high confidence)**

10. Lowering the fuel aromatic content reduces the aircraft soot particle number and mass emissions, whereas lowering the fuel sulphur content reduces the vPM number emissions. **(very high confidence),**

11. PM EI (number and volume) reduction is predominantly a function of fuel sulphur and aromatic content in RQL combustors tested at high TRL by NASA and presented in the work of Moore et al. [53] this is the highest fidelity testing of its kind. **(high confidence)**

12. PM EI content has been demonstrated at low TRL to be a function of aromatic speciation and structure, not only total aromatic content. **(medium confidence at engine conditions)**

13. Lean burn combustion test rigs have investigated the effect of FT synthetic jet fuel on PM and other emissions as well as fuel atomisation at a range of representative power settings in low TRL rigs (~TRL 3). With the limited data available, Hicks et al [120], and Okai et al [159], it would appear that PM emissions in lean burn combustors are primarily produced by the rich pilot flame, and that higher pilot splits are likely to produce greater PM number and mass emission concentrations than low pilot splits, particularly when running globally richer mixtures at higher power conditions. **(high confidence)** Back to back results for lean burn and rich burn systems across the full range of power settings are not available. **(low confidence)**

14. Similar reductions in PM mass and number were seen for lean burn pilot only combustion and conventional combustion systems. **(high confidence)**

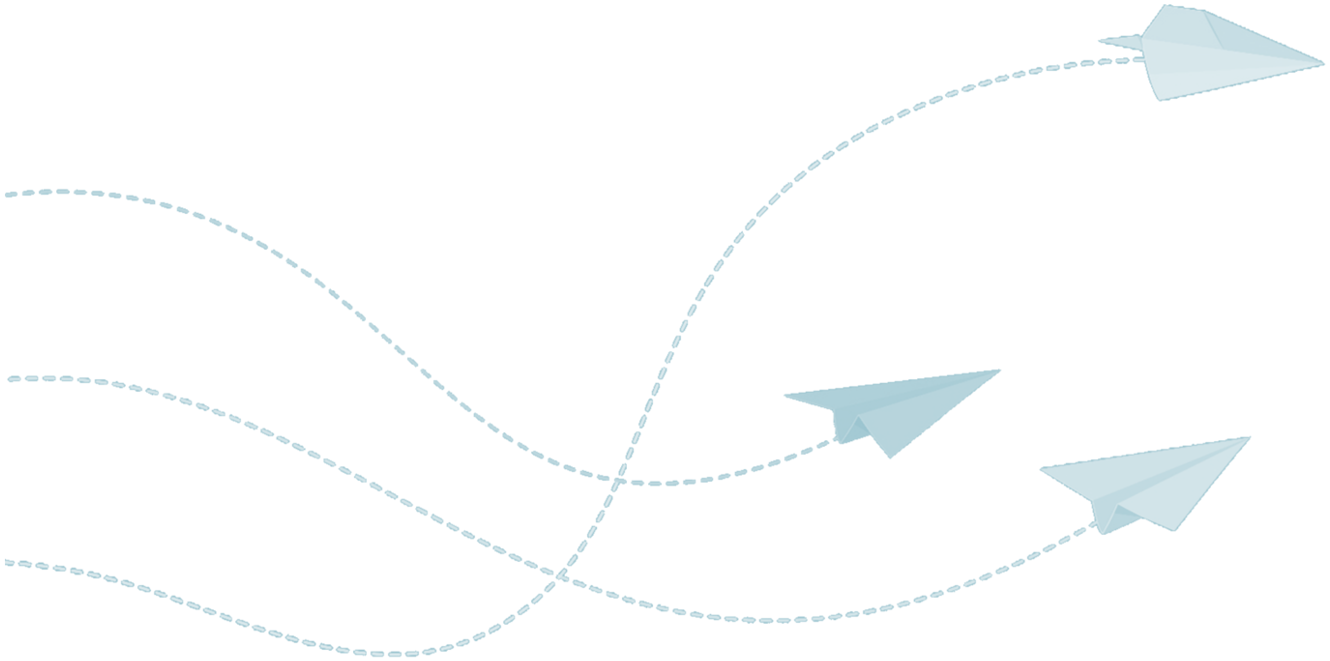
15. Lean burn low pilot splits only appear to generate notable PM emissions for mid to high power, higher global fuel equivalence ratios, in particular with higher pilot split for mid power – e.g. 20% pilot, 80% main, rather than 10% pilot 90% main. This is a consequence of pilot split and fuelling strategy for a given lean burn system. Fuel split and lean burn staging strategy will of course need to be balanced with other combustor operating parameters to maintain combustor operability and robust combustion stability/life. Changing to low aromatic content fuels at this condition reduces PM emissions considerably. **(high confidence)**

16. Change in lean burn combustor flow field recirculation, with reactions taking place in different locations, showing a longer pilot flame zone but earlier ignition. This warrants further work as changes in heat release location will change combustor liner/tile life in addition to changes in fuel spray nozzle wetted wall temperature and potentially limit life in both of these components [107]. This will also depend on flame luminosity which is a factor of carbon emissions, requiring well instrumented tests to understand these effects. **(medium confidence)**

17. The hypothesis postulated by Lieuwen et al. [104] that lean burn combustion system PM emissions are likely more sensitive to low aromatic fuel content may require further investigation based on

the limited low TRL experimental test data available in the current open literature. Similarly, arguments put forward regarding superior performance of cross flow atomiser lean burn injectors currently appears to be incorrect for low TRL systems as demonstrated by the work in air blast atomisers carried out at JAXA by Okai et al. [120]. This, of course warrants further work at higher TRL levels using a range of fuel atomiser architectures and operating conditions with high TRL emission measurement instrumentation suites, such as those used in the NASA-AAFEX and ECLIF programs. Testing at this level would allow for an effective comparison between state-of-the-art lean burn combustion systems and current RQL combustion systems, allowing a conclusive consensus to be drawn. **(medium confidence)**

18. Based on the reviewed literature, air-blast atomisers show no trend in droplet size between conventionally sourced Jet – A and FT synthetic jet fuel with low aromatic content. Conversely, pressure swirl atomisers do exhibit a change in droplet size, with FT Synthetic jet fuels producing smaller mean diameter droplets and a larger distribution of small droplets. This trend increases with reduced operating power in the APU tested. **(medium confidence)**



6. The effects of aviation emissions of soot as they relate to contrails and cirrus clouds and changes with fuel composition

Summary

This chapter deals with the underlying atmospheric science associated with contrails – their formation, influence on cloudiness, uncertainties and the influence of technology and fuel composition. Contrails are presently understood to be the largest of aviation's current non-CO_2 warming effect on climate, but this is subject to change, both in terms of the stability of the estimates of effective radiative forcing (a measure of how large the effect is on climate), and improvements in the modelling (which is limited to only two current models that account for water vapour feedbacks). The estimate of scientific confidence level in the contrail cirrus effect is 'low'. Only long-lasting 'persistent' contrails that spread into contrail cirrus with lengths/widths of the order >100 km have a significant forcing effect. For current fossil fuels, and RQL engines (95% of the global fleet), soot emissions remain an important determinant of the occurrence of contrails and their lifetime since soot forms the nuclei on which ice crystals are formed. Associated with the underlying aircraft soot emission, is the so-called 'indirect' effect, whereby the properties of naturally occurring cirrus can be modified. There is no best estimate of the size of this effect, but consensus is emerging that it is potentially negative (cooling). Some research indicates a sizeable negative forcing (greater than contrail cirrus positive forcing), other work suggests that it could be negligible. Fuel composition has been shown to have an influence on soot number emissions from aircraft engines, with aromatics, and in particular, di-aromatics being largely – but not solely – responsible. Many ground-level and a few high-altitude measurements have demonstrated a reduction in soot number with increasing SAF or semi synthetic content blends; synthetic blend components and SAF typically have zero to no aromatics, so is a good indicator of what may happen with aromatic-reduced fossil fuel. There are a limited number of high-altitude measurements (essentially one measurement campaign) that show reduced ice crystal numbers from SAF fuel. However, all the measurements tend to be from RQL engines. Lean burn engines have the potential to reduce soot number emissions by orders of magnitude rather than tens of percent, largely eliminating soot. However, modelling work indicates that ice crystal number is reduced with decreasing soot number emission, but below a critical threshold (where 'lean burn' may start) ice crystal number may increase again, forming on much smaller volatile particles in the exhaust, i.e. in the absence of the larger competing larger soot particles. Much of this aforementioned science is highly uncertain and requires much more integrated research to scope all these issues to reduce uncertainty. This chapter also outlines the complex issues inherent in 'trading' a potential reduction in (a rather uncertain) contrail forcing from modified fuel composition with the consequential increased CO_2 emissions incurred at the refinery to process (hydrotreat/hydrocrack) the fossil fuel. Contrails/contrail cirrus is a very short-term radiative effect that disappears almost instantaneously on the contrail being removed (by sublimation – ice to gas phase transition of water), whereas a significant fraction of any extra CO_2 emission has a radiative effect from centuries to millennia. This complicates any evaluation of whether fuel mitigation of aromatics actually benefits the climate or not, since timescales have to be considered.

6.1. Introduction

The premise of this study is to examine the potential environmental benefits and/or disbenefits of removing/reducing aromatic compounds present in fossil-based aviation fuel (mostly, Jet A-1, see Chapter 3). As outlined elsewhere in the report, aromatic compounds present in jet fuel (see Chapter 3) are empirically observed to be responsible for some fraction of aircraft soot emissions (Chapter 5). For current fuels and combustor technologies, soot particles form the non-volatile core on which water vapour may condense in the hot exhaust, which subsequently freeze at cruise-type altitudes, and if the surrounding air is supersaturated with respect to ice, form a persistent contrail, which can affect climate, exerted through changes in the radiative balance of the atmosphere ('radiative forcing') [160], [58].

In this chapter, we outline the mechanism of the formation of contrails, their dependency on both fuel composition and combustion conditions, and the potential radiative impact of persistent contrails.

In order to address whether an environmental benefit in terms of climate can be gained from reducing the aromatic content of fuel, and potentially contrails, a number of questions need to be asked:

1. What is the size of the 'contrail effect' in terms of the effective radiative forcing, the metric commonly used for quantification and comparison of different effects? What are the associated uncertainties, is the effect sufficiently well-characterised and which parts of the science are still evolving?

2. What change in soot emissions and consequential radiative forcing may arise from a reduction in the aromatic content of fossil fuel? How certain is this? What is the evidence base?

3. What increase in terms of life-cycle emissions of CO_2 might be involved in the extra processing of aviation kerosene at the refinery to reduce aromatic content?

4. If an increase in the life cycle emissions of CO_2 is involved, then what equivalency approach should be used to balance the potential reduction of the radiative impacts of persistent contrails against increased CO_2 emissions?

Overview of processes

6.2. Contrail formation

Condensation trails – 'contrails' – have been observed to form behind aircraft flying at altitudes > 8 km since 1918 [161] and more extensively during WWII, as the altitudes at which aircraft flew increased [162]. In response to interest in the potential of contrails to adversely affect climate, much research has been undertaken over the last three decades. The formation of contrails can be described thermodynamically, by the 'Schmidt-Appleman criterion' [163]. This requires knowledge of the isobaric heat capacity of air, ambient pressure, the emission index of water vapour, the overall propulsion efficiency of the aircraft and combustion energy per unit mass of the fuel. This description of initial formation requires no details of microphysical conditions or criteria, essentially assuming an abundance of particles that serve as condensation nuclei and air temperatures below the formation threshold of approximately -40 °C (~233 K). These thermodynamic parameters can predict, with good confidence, the formation of contrails and their degree of persistence[3], but not their lifetime, how they transition to contrail cirrus or their ultimate climate impact.

Contrails are line-shaped clouds of ice crystals formed from water vapour from the exhaust of aircraft that condenses on aerosols formed within the engine and plume, and entrained aerosol which may subsequently freeze, which grow in size from ambient water vapour. 'Volatile' and 'non-volatile' aerosol particles (vPM and nvPM) are formed within the combustion chamber of the engine and the immediate plume. Strictly speaking, nvPM is a carefully designed ground-level regulatory measurement for ICAO-CAEP emission standards for mass and number. The nature of nvPM is otherwise often described as 'soot' and vPM as ultrafine aqueous particles (UAPs) from sulphur, condensable organics and ionised gases [160]. For current fuels and engines, contrail ice crystals are mostly formed on soot particles. This is represented in Figure 6.1 for the jet and vortex regimes. Ice crystals that persist into the vortex regime tend to be forced downwards, leading to sublimation of a fraction of the total in the lower part of the plume. The ice crystals that persist in the upper part of the plume may grow under ice supersaturated conditions.

Line-shaped contrails, if long-lived (>10 mins; [164]), may then spread by windshear and turbulence, transitioning into contrail cirrus, losing their original shape. The cirrus cloud formed may merge with natural cirrus and be advected 10s to 100s of km. The resultant clouds may then change the radiative properties of the atmosphere by adding cirrus-like clouds.

Eventually, the ice crystals will sublimate in warmer drier air, releasing the soot cores once more and these may go on to alter natural cirrus cloud properties, and/or be removed from the atmosphere to the earth's surface by dry and wet deposition processes.

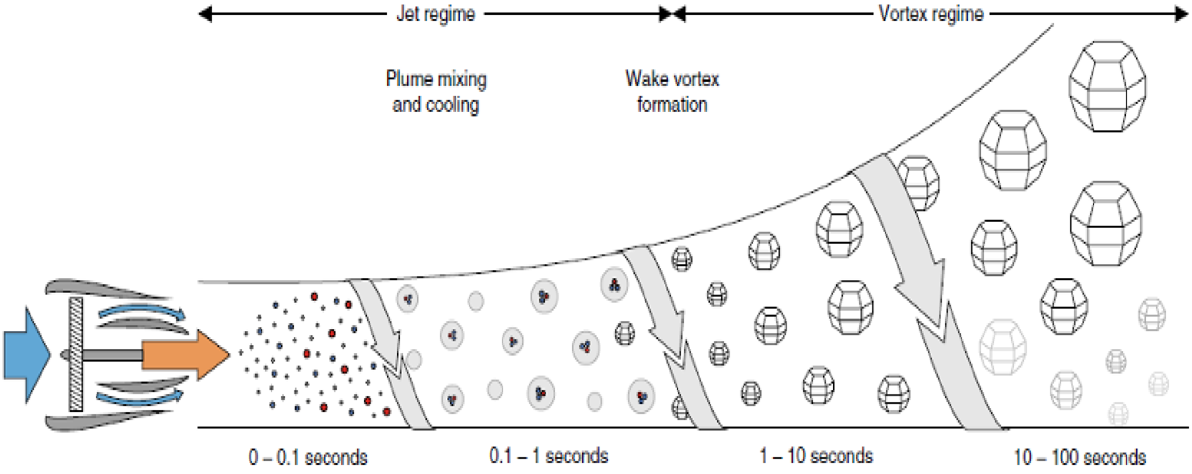


Figure 6.1: The formation of ice crystals in the exhaust of aircraft engines at cruise altitudes for ambient conditions of -40 °C during the jet and vortex regimes (from Kärcher, [160]). Particles comprise soot, Ultrafine Aqueous Particles (UAPs) and entrained ambient particles.

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[3] *Contrails may form and 'persist' (not immediately sublimate) if the ambient air is saturated with respect to ice. So, a long line-shaped contrail of 10s of km may be persistent, but in practice has little or no radiative effect since it has not spread [160]; lifetime simply refers to how long it persists - it may be minutes or hours.*

A physical process model developed by Kärcher and Yu [165] relates soot particle number concentration in the exhaust to the number of ice crystals formed (Figure 6.2). In the current soot rich regime, the number of ice crystals is approximately linearly related to the number of soot particles and also increases with colder ambient temperatures. This relationship has been empirically observed in the real world for high soot concentrations (e.g. Voigt et al. [166]). At low soot numbers the model indicates that given sufficiently cold temperatures a higher number of ice particles might form on ultrafine water drops. This has not yet been observed and this process model is unconstrained by observations in the low soot regime.

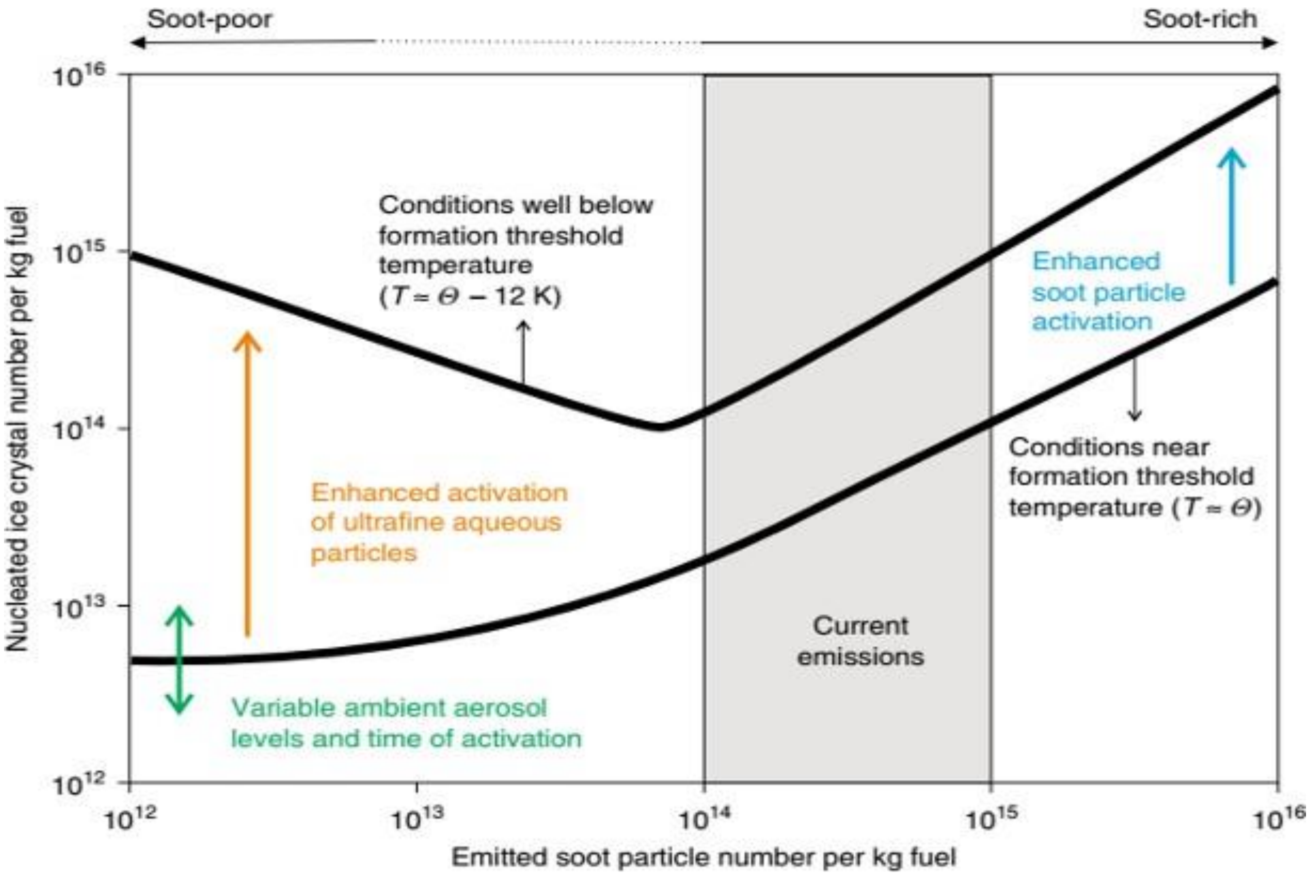


Figure 6.2 Modelled dependence of ice crystal number per kg fuel vs soot particle number per kg fuel for temperature conditions close to the threshold temperature of formation, and 12K lower (from Kärcher [160])

6.3. The effective radiative forcing of persistent contrails and contrail cirrus

The way in which persistent contrails and contrail cirrus can affect the instantaneous radiative balance of the atmosphere is shown in Figure 6.3 and is the balance of solar (short wave) and terrestrial (infrared, long wave) radiation fluxes. At night, outgoing infrared radiation is trapped, resulting in warming; during the daytime, incoming solar radiation may be additionally reflected back to space (a cooling effect) balanced by infrared radiation trapping by the cloud. The net balance during the day may be warming or cooling, depending on factors such as ice crystal size, shape, density, solar zenith angle and underlying/overlying (other) cloud cover. At dawn and dusk, when the sun is low in the sky, the net balance is mostly negative with solar scattering and reflection being at its most effective. Thus, to know the net balance of a contrail, its lifetime (and evolving physical characteristics) must be considered and quantified, since the net sign can switch from positive to negative and vice versa, depending on time of initial formation and lifetime (e.g. Wang, [167]. The radiative balance is usually calculated with complex radiative transfer models that consider all these physical parameters (e.g. Myhre et al., [168]).

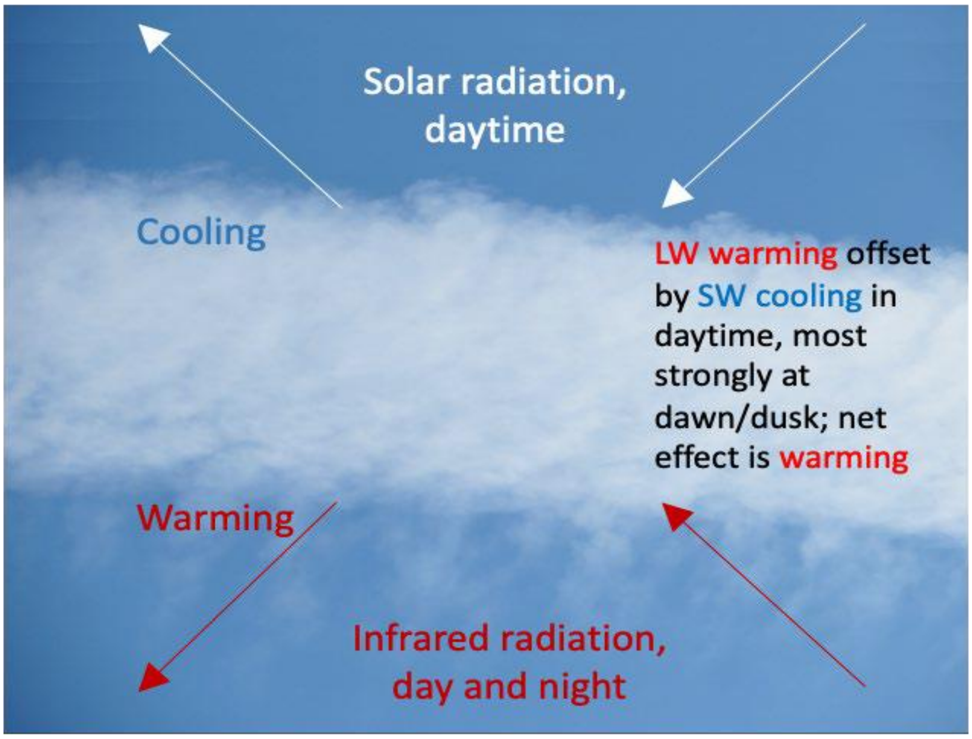


Figure 6.3 Instantaneous radiative effects of a contrail at different times of day/night

In the above description, the ‘instantaneous radiative forcing’ has been considered, the change in the radiative balance of the atmosphere without any feedbacks. As a concept, ‘radiative forcing’ of climate has been the most widely used to date to quantify effects on climate, which has been expanded to ‘effective radiative forcing’. In the following, a brief description of these concepts and their rationale is provided.

Radiative Forcing (RF) has units of watts per square metre (W m^{-2}) and is a measure of the perturbation of the planetary radiation budget owing to some effect, e.g. increases in greenhouse gas concentrations, aerosol change, human-induced cloud change, relative to a pre-industrial state. With the concept, the climate system responds to the RF resulting in a new equilibrium surface temperature change, that would be higher than that measured over a pre- industrialization period if the net RF is positive. This concept allows a comparison of the size of different effects that change climate. RF is proportional to the equilibrium surface temperature change relative to (say) pre-industrial temperature (T-Tpi), that would result if that RF was applied for many decades, so that:

$$T - T_{pi} \gg \frac{RF}{\lambda} \qquad (6.1)$$

where the constant of proportionality, **λλ**, is the *equilibrium climate* feedback parameter in W m^{-2} K^{-1}. The value of **λλ** is a major uncertainty in climate science owing to uncertainty in the way clouds respond to climate warming (see also Box 7.1 of Forster et al.,[169]) and is dependent on physical properties of the climate system. In earlier IPCC reports, because of the complexity and computational resource requirements of calculating a new equilibrium temperature response, and the uncertainty in **λλ**, RF has been the favoured metric as a proxy for a change in global mean surface temperature response (DT) and has previously been calculated offline from global climate models. More recently, advances in the science that have shown that **λλ** may also be effect dependent. For example, in the above equation, it is assumed that the global-average temperature change from, for example, a 1 W m^{-2} perturbation due to contrails, is similar to that resulting from 1 W m^{-2} due to aviation-induced CO$_2$ changes. However, climate model experiments have shown that this is not necessarily true. Nevertheless, because the RF of aviation induced effects are small compared with other signals, RF estimates are heavily used within the research community, as it is often challenging to see a statistically robust signal of the impact of aviation on climate within other climate indicators such as global mean temperature change.

The Fifth and Sixth IPCC assessments adopted effective RF (ERF) as the preferred measure, as it incorporates adjustments resulting from an RF (e.g., in cloudiness) that occur on a more rapid timescale than resulting surface temperature changes (which occur over periods of decades), see Figure 6.5. For some climate forcing agents such as CO$_2$, the difference between RF and ERF is small (order 10%). For others, notably contrails, the results from the very few model experiments available [170], [171], [172] show that there is model to model variability but a consensus that the ERF is around half the RF [58]. This may be due to the RF mostly exerting itself in the upper troposphere where it is less impactful.

There is also the additional significant consideration as to how ERF is calculated. If only the short- term effects of e.g. cloud and water vapour adjustments (in the case of contrails) are considered (example c, in Figure 6.4 below), then this may differ significantly from the full equilibrium temperature response, which is calculated with a coupled ocean-atmosphere model [173].

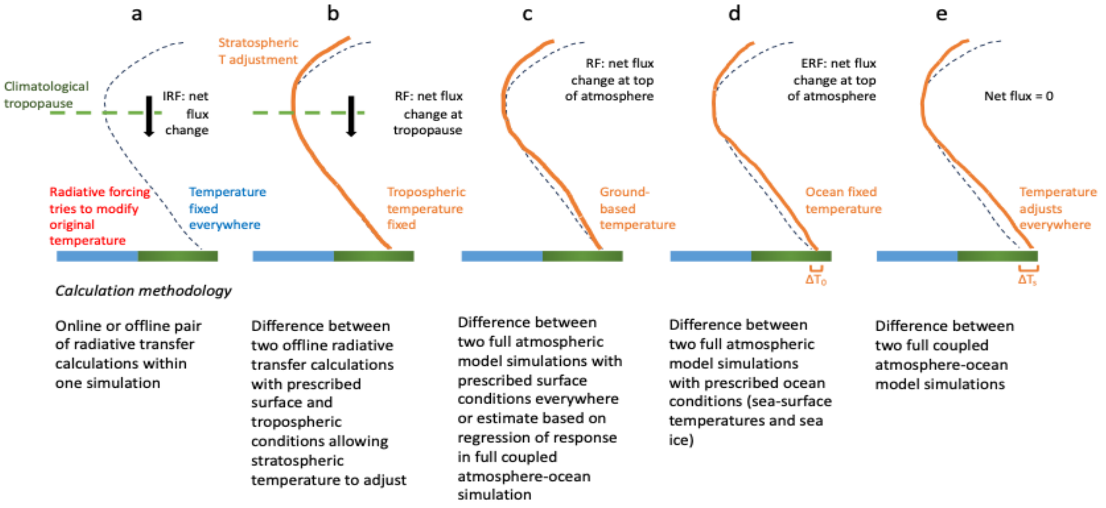


Figure 6.4 Schema comparing (a) instantaneous RF (IRF), (b) RF, which allows stratospheric temperature to adjust, (c) flux change when the surface temperature is fixed over the whole Earth (a method of calculating ERF), (d) the ERF calculated allowing atmospheric and land temperature to adjust while ocean conditions are fixed and (e) the equilibrium response to the climate forcing agent. The methodology for calculation of each type of forcing is also outlined.
DT0 represents the land temperature response, while DTs is the full surface temperature response. Based on [168]

A recent assessment of the effect of contrails and contrail cirrus compiled model results, carefully normalizing the results, and where possible, the methodological assumptions so that a multi model assessment could be made [58]. The results are reproduced in Figure 6.5.

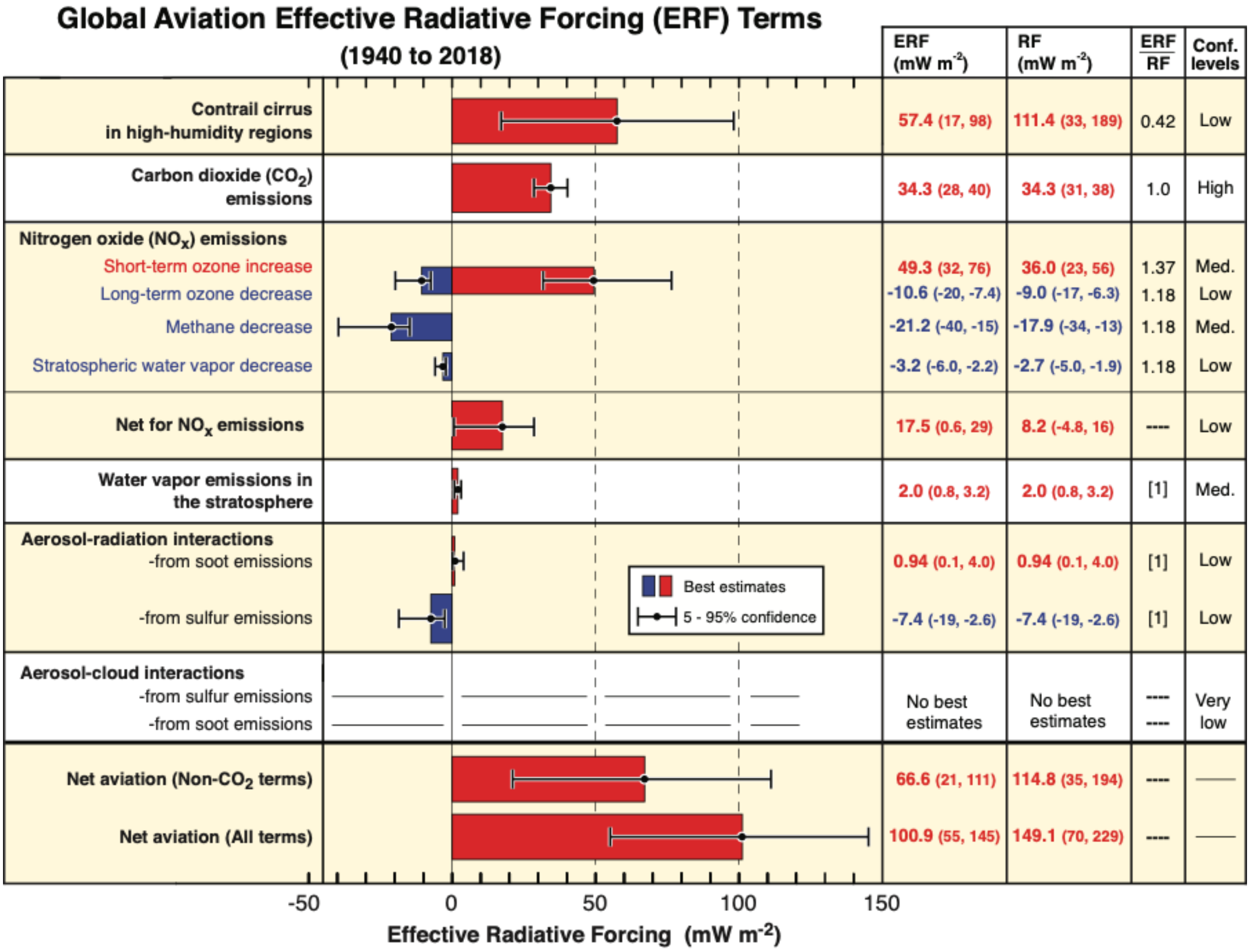


Figure 6.5. Best-estimates for effective radiative forcing (ERF) terms from global aviation from 1940 to 2018.

The bars and whiskers show ERF best estimates and the 5–95% confidence intervals, respectively. Red bars indicate positive terms and blue bars indicate negative terms. Numerical ERF and RF values are given in the columns with 5–95% confidence intervals along with ERF/RF ratios and confidence levels. RF values are multiplied by the respective ERF/RF ratio to yield ERF values. ERF/RF values designated as 1 indicate that no ERF/RF estimate is available yet. Taken from Lee et al. [58]

The uppermost bar in Figure 6.5 represents the best available multi-model assessment of ERF (and RF) from “contrail cirrus in high humidity regions” (57 mW m^{-2}, 17–98 mW m^{-2} uncertainty range). This multi model estimate includes long-lived contrails and a contrail cirrus. It is important to understand the relative importance of these rather poorly defined sub-components. Based on a review of the literature, [160] suggested that short-lived contrails (<10 mins) are of negligible importance, whereas longer-lived contrails (10 mins to hours) are of “small” importance to RF. These definitions effectively apply to any line-shaped contrail and hence should be considered in terms of operational satellite detection, which is currently limited to line- shaped structures. It is the irregularly shaped contrail cirrus cloud that is considered to comprise approximately 80% of the forcing [174].

A number of points need to be made regarding the absolute and relative sizes of the ERF values and their uncertainties in figure 6.5. This is critical in the consideration of the potential benefits (or otherwise) of aromatic reductions in fossil fuel. The underlying RF values originate from only three climate models (two variants of ECHAM e.g.[175], CAM5 e.g. [176], CAM3+–IMPACT e.g. [177] with COCIP e.g. [178]). These are all models that generate their own meteorological data (climate models) with closed water vapour budgets. Such a low number of models represents a poor characterization of the issue. Of these models, only one is in current development (ECHAM) and CAM5 has only been used once since Chen and Gettelman's [176] estimation of RF, for the COVID- related reductions in air traffic [179]. The COCIP model [178] differs since it is a diagnostic scheme that uses external meteorological data, and in its self-standing state, i.e. in the absence of being subsumed into a climate model, does not calculate contrails in a closed water vapour budget (so cannot be used to calculate an ERF).

The uncertainties apply to the calculated RF value. The ERF/RF adjustment was made on the basis of only three model simulations, and the uncertainties of this were not combined with the underlying uncertainties of the RF estimates, such that the uncertainties of the ERF values quoted are likely underestimates. More recent modelling using ECHAM has incorporated a parameterization of the loss of ice crystals in the wake vortex owing to sublimation from the downwards forcing of the plume, resulting in a 22% reduction of the previously calculated RF [180], demonstrating that incomplete process representation can result in significant changes.

The uppermost bar in Figure 4.5 represents the best available multi-model assessment of ERF (and RF) from "contrail cirrus in high humidity regions" (57 mW m^{-2}, 17–98 mW m^{-2} uncertainty range). This multi model estimate includes long-lived contrails and a contrail cirrus. It is important to understand the relative importance of these rather poorly defined sub-components. Based on a review of the literature, [160] suggested that short-lived contrails (<10 mins) are of negligible importance, whereas longer-lived contrails (10 mins to hours) are of "small" importance to RF. These definitions effectively apply to any line-shaped contrail and hence should be considered in terms of operational satellite detection, which is currently limited to line- shaped structures. It is the irregularly shaped contrail cirrus cloud that is considered to comprise approximately 80% of the forcing [174].

6.4. Impact of fuel properties on contrails

Contrail formation

Contrails can form behind an aircraft when the hot and humid exhaust plume mixes with colder ambient air, leading to rapid cooling and can cause the plume to be water supersaturated. When conditions in the exhaust plume are supersaturated with respect to water, water vapour can condense onto the surface of emitted and/or ambient particles found within the plume to form water droplets, which subsequently grow and freeze to form contrail ice crystals [163], [165]. The contrail formation process is typically described using the Schmidt-Appleman criterion (SAC) [163], which was derived based on the theory of thermodynamics, and assumes that contrails form when the ambient temperature falls below the SAC threshold temperature (TSAC),

$$T_{SAC}\left[K\right] = (273.15 - 46.46) + 9.43\ln\left(G - 0.053\right) + 0.72\left[\ln\left(G - 0.053\right)\right]^2 \tag{6.1}$$

where G is the gradient of the mixing line in a temperature-humidity diagram

$$G = \frac{EI_{H_2O}p_{amb}c_pR_1}{LCV(1-\eta)R_0} \tag{6.2}$$

p_{amb} is the pressure altitude at each waypoint, c_p is the isobaric heat capacity of dry air (1004 J kg^{-1} K^{-1}), and R1 (461.51 J kg^{-1} K^{-1}) and R_0 (287.05 J kg^{-1} K^{-1}) are the gas constant for water vapour and dry air respectively. LCV is the energy content per unit mass of the fuel, *h* the overall propulsion efficiency and EI H_2O is the emissions index of water vapour.

The SAC has been extensively compared with observations [56], [177], [181] and is widely used in experimental campaigns to identify regions that are forecast to form contrails [54], [166], [182], [183], and in contrail models to initialise contrail formation [176], [178], [180],[184].

Based on the SAC, c.f. Eq. (6.1) and (6.2), lowering the volume of fuel aromatic compounds is expected to impact the contrail occurrence in two ways: (i) it increases the fuel hydrogen mass content, a factor that is positively correlated with the EI H_2O, resulting in a larger G, and TSAC; and
(ii) it also increases the fuel LCV in line with the variation in molecular structure as discussed in Chapter 2 and Chapter 3, which in turn lowers G and TSAC. On average, the compiled fuel database (Table 1 and Figure 1) suggests that lowering the volume of fuel aromatic content (from 20% to 0%) results in a 12% increase in fuel hydrogen content (and EI H_2O) and a 3% increase in fuel energy content per unit mass, thereby increasing TSAC by up to 0.5 K. This analysis indicates an increased likelihood of contrail formation from low- and zero-aromatic fuels compared to conventional fuels. When informed by these changes, three regional contrail simulation studies estimate a 1–8 % increase in contrail occurrence resulting from the use of low-aromatic SAF [143], [184], [185].

We note that the number of particles emitted by the aircraft is not an input parameter to the SAC because there will always be particles in some form that are present in the exhaust plume that can serve as condensation nuclei. These include: (i) nvPM which typically range from 10^{14} to 10^{16} kg^{-1} for aircraft-engine types powered by RQL combustors [123]; (ii) vPM with EI_n that ranges between 10^{16} and 10^{17} kg^{-1} [56]; and (iii) ambient aerosols which concentrations are generally two to three orders of magnitude lower than the nvPM [186].

While the number of particles is not expected to influence the contrail formation phase, the FSC may lead to minor changes. An early experimental campaign found minor differences when visually observing contrails that were formed from fuels with a low and high FSC (170 vs. 5500 ppm) [163], [187]. In this experiment, contrails from the high-sulphur fuel: (i) started to be visible earlier at around 10 m behind the engine exhaust, compared to 15 m for contrails formed by the low-sulphur fuel; and (ii) started forming at slightly higher temperatures (0.2 – 0.4 K) than those from the low-sulphur fuel. These observations can most likely be attributed to the role of H_2SO_4 in coating the surface of soot particles, which can increase the soot hygroscopicity, thus slightly reducing the critical water saturation ratio and facilitating the activation of soot to form water droplets PM [152], [153], [154]. Although these effects are not currently accounted for in the SAC, they may be negligible, as a substantial change in FSC (from 170 ppm to 5500 ppm, well above the regulatory limit of 3000 ppm) only resulted in a small change in TSAC (< 0.4 K) [188].

Young contrail properties

Both the fuel aromatic and sulphur content contribute to the total number of aircraft PM emissions via different pathways: the fuel aromatic content is positively associated with the soot EI_n (Chapter 5); while the fuel sulphur content adds to the vPM EI_n and can also coat the surface of soot particles which increases its hygroscopicity and activation efficiency to form water droplets (Chapter 6).

Results from parcel model simulations suggest that the initial contrail properties are strongly influenced by the aircraft particle number emissions [165], [189]. In the 'soot-rich' scenario where the soot EI_n is thought to be greater than 10^{14} kg^{-1}, the soot primarily acts as the source of condensation nuclei causing the soot EI_n to be positively correlated with the initial contrail ice crystal number and optical depth and negatively correlated with the initial contrail ice crystal size. However, in the 'soot-poor' scenario (soot EI$_n$ < 10^{14} kg^{-1}), vPM and ambient aerosols can nucleate to form contrail ice crystals and, depending on the ambient temperature and aerosol concentration, the initial contrail ice crystal number could be up to three orders of magnitude larger than the soot EI$_n$.

Earlier experimental campaigns that measured the effects of FSC on young contrail properties showed that the number of ice crystals in young contrails was approximately equal to the number of soot particles when the FSC is low (< 170 ppm); and (ii) increased slightly by 30% when the FSC was increased significantly from 6 to 2800 ppm, suggesting that a small fraction of vPM may have nucleated to form contrail ice crystals [56]. The vPM EI$_n$ within contrail plumes were around 2 to 8 times less than equivalent measurements in dry exhaust plumes for both low and high FSC of 22 and 2700 ppm respectively, thereby suggesting that a large fraction of vPM were likely scavenged by the contrail ice crystals [157]. In addition, contrails formed from a very high sulphur fuel (5500 ppm) was also observed to have a larger optical depth and sublimated more quickly than those formed from a low sulphur fuel (170 ppm) [163]. These observations point to a greater number of smaller ice crystals within the contrails formed from the high sulphur fuel relative to the contrails formed from the low sulphur fuel [163], [187].

Table 6.1: Compilation of the measured nvPM EI$_n$, contrail AEI, the activation rate of nvPM to form contrail ice crystals (activation), and the mean contrail ice crystal radius resulting from the use of fuels with different aromatic content. The values in the parentheses represent the percentage change in contrail properties relative to the conventional Jet A-1 fuel.

Campaign	Fuel	nvPM EI$_n$ (×10^{14} kg^{-1})	Contrail AEI (×10^{14} kg^{-1})	Mean $f_{activation}$	Mean contrail ice radius (μm)
	Jet A-1 (Ref2)	49 ± 6	42 ± 6	0.86	1.9
Campaign	Fuel	nvPM EI$_n$ (×10^{14} kg^{-1})	Contrail AEI (×10^{14} kg^{-1})	Mean $f_{activation}$	Mean contrail ice radius (μm)
ECLIF I & ECLIF II/ND-MAX[1]	SSF1 SAJF1 SAJF2	25 ± 2 (-49%) 27 ± 6 (-45%) 23 ± 6 (-53%)	20 ± 2 (-52%) 23 ± 2 (-45%) 11 ± 4 (-74%)	0.80 0.85 0.48	2.7 (+42%) N/A N/A
ECLIF II/ND-MAX[2]	Jet A-1 (Ref3) SAJF1 SAJF2	25 ± 7 20 ± 4 (-20%) 17 ± 4 (-32%)	21 ± 5 16 ± 4 (-24%) 13 ± 3 (-38%)	0.84 0.80 0.76	0.86 0.93 (+8.1%) 0.87 (+1.1%)
ECLIF III[3]	Jet A-1 100% HEFA-SPK	10.3 ± 3.0 6.4 ± 0.7 (-38%)	8.7 ± 4.0 3.9 ± 1.5 (-55%)	0.84 0.61	N/A N/A

[1] [166], [2] [182], [3] [54]

More recently, two experimental campaigns measured the change in nvPM and its corresponding contrail properties resulting from the use of conventional fuel and SAF with different fuel aromatic contents [54], [166], [182]. As the engines powering the aircraft were RQL combustors, the nvPM EI$_n$ for all data points were above 10^{14} kg^{-1} and remained in the 'soot-rich' scenario. Their measurements showed consistency with the model simulations, where the use of SAF with low- or zero-aromatic content lowered both the nvPM EI$_n$ by 16–53% and the contrail apparent emissions index (AEI, i.e., the number of contrail ice crystals formed per mass of fuel burn) by 24– 74% relative to conventional fuels (Table 6.1). For each data point, the contrail AEI is reduced more strongly than the nvPM EI$_n$ which is most likely caused by a combination of factors, including: (i) adiabatic heating during wake vortex downwash causing a fraction of freshly formed contrail ice crystals to sublimate; (ii) the lower relative aromatic content in SAF resulting in smaller nvPM sizes; and the lower relative FSC in SAF which could reduce the (iii) vPM EI$_n$; (iv) vPM size; and (v) nvPM hygroscopicity. Factors (ii), (iv) and (v) consequently necessitates a higher plume water saturation ratio for the nvPM and/or vPM to activate to form water droplets, which likely reduced the fraction of particles that formed contrail ice crystals. The contrails formed by low- and zero- aromatic SAF were also measured to have larger ice crystal sizes and smaller optical depths relative to contrails formed from conventional fuels under comparable atmospheric conditions.

Overall, the findings from the experimental campaigns mentioned in Chapter 5 were generally consistent with model simulations. However, it is important to highlight that all contrails examined in these campaigns were formed under 'soot-rich' conditions, and additional measurements are necessary to investigate the potential differences in contrail properties when they are formed in the 'soot-poor' scenario. To address this gap, further experimental campaigns such as the Boeing ecoDemonstrator [190] and Airbus VOLCAN [191] campaigns are currently ongoing. The findings from these campaigns will provide new insights into contrails formed by cleaner lean-burn engines powered by both conventional fuel and SAF.

6.5. Effects on aviation climate forcing

Aircraft particle emissions

Soot and sulphate particles emitted by aircraft engines at cruise altitudes cause a direct climate effect by interacting with the incoming solar and/or outgoing terrestrial radiation [192], [193]. Soot particles, primarily composed of black carbon, are darker in colour and exhibit a strong absorption capacity for both incoming short-wave radiation and outgoing long-wave radiation, thereby contributing to a net warming effect. In contrast, sulphate particles are typically lighter in colour and tend to scatter incoming solar radiation, resulting in a net cooling effect. On aggregate, the scientific consensus indicates that the direct climate effect of soot yields a small positive radiative forcing (RF) of 0.94 [0.1, 4.0] mW m^{-2} (5% - 95% confidence interval) in 2018, whereas the direct climate effects of sulphates is estimated to have a negative RF of -7.4 [-19, -2.6] mW m^{-2} [58].

In addition, both soot and sulphate particles can also contribute to an indirect climate effect by modifying the properties of contrails and natural cirrus [165] [194], [195]. More specifically, these particles found in the engine exhaust can act as condensation nuclei for contrail formation which:
(i) influences various young contrail properties such as the initial ice crystal number, size, and optical depth (Section 4.2), which may subsequently change its magnitude of climate forcing over their lifecycle (as will be discussed in Chapter 7); and (ii) possibly, dehydrate the atmosphere and change the natural cirrus occurrence and coverage area in regions with high air traffic density [172], [195], [196]. These particles are also thought to have differences in their ability to interact with natural clouds: (i) sulphates serve as cloud condensation nuclei to facilitate the formation of liquid clouds and increase its optical depth; (ii) freshly emitted aircraft soot particles do not appear to be efficient condensation nuclei for cirrus clouds; but (iii) soot that was previously activated to form contrail ice crystals can act as cloud condensation nuclei via pore condensation and freezing mechanism [197], [198], [199], [200]. However, due to the complexities inherent in aerosol-cloud interactions, there is currently no scientific consensus on the best estimate of the RF from these indirect effects. Among the limited number of studies that have attempted to estimate the climate forcing from these indirect effects, their net RF estimates varies widely and range from a large negative RF (up to -300 mW m-$^{2)}$ [201], [202], [203] to a small positive RF (up to 13 mW m^{-2}) [176], [204], [205].

Persistent contrails

Several studies have utilised contrail models to evaluate the sensitivity of the contrail properties and climate forcing over its lifecycle to inputs of aircraft particle number emissions (Table 6.2). While no studies to date have specifically investigated the effects of fuel hydrotreatment on the contrail climate forcing, we extrapolate these findings and assume that the reduction in aircraft particle number emissions through fuel hydrotreatment would yield similar outcomes.

Table 6.2: Summary of the different global and regional modelling studies that evaluated the percentage change in contrail net RF resulting from the change in soot EI_n.

Study	Region (Year)	Contrail model	Soot EI_n	Contrail net RF	Remarks
Schumann et al.[1]	Global (2006)	CoCiP	+100%	+60%	Sensitivity analysis of the soot EI_n and contrail ice crystal number on the global annual mean contrail net RF.
Caiazzo et al.[2]	USA (2006)	CERM	-75%	(-4, +18)%	Investigated the effects on biofuels on the contrail climate forcing, Reported change in contrail net RF likely represents the local contrail net RF, i.e. the change in radiative flux over the contrail area. The range in contrail net RF' was derived from different assumptions of contrail ice crystal habits.
Burkhardt et al.[3]	Global (2006)	ECHAM5	-80%	-50%	Investigated the effects on contrail climate forcing resulting from an 80% reduction in soot EI_n,
Bock & Burkhardt[4]	Global (2050)	ECHAM5	-50%	-15%	Assume background climate in 2050, Assume the use of future aircraft (with improved fuel and propulsion efficiency) and alternative fuels (with lower soot EI_n and higher EI H_2O)
Teoh et al.[5]	North Atlantic (2019)	CoCiP	-52%	-44%	Fleetwide adoption of 100% SAF Reduction in soot EI_n due to SAF estimated from a parametric model
Bier & Burkhardt[6]	Global (2006)	ECHAM5	-80%	-41%	Investigated the effects on contrail climate forcing resulting from an 80% reduction in soot EI_n, Update to Burkhardt et al.(Burkhardt et al., 2018) Accounts for variabilities in soot activation rate and ice crystal losses in the wake vortex phase.
Markl et al.[7]	Global (2006)	ECHAM5	-60%	-26%	Fleetwide adoption of 100% SAF Assumed reduction in soot EI_n informed by in-situ measurements

[1] [142], [2] [184], [3] [206], [4] [207], [5] [143], [6] [180], [7] [54]

According to model simulations, lowering the aircraft particle number emissions and initial contrail ice crystal number in the 'soot-rich' scenario generally leads to larger ice crystal sizes and optically-thinner contrails relative to the baseline scenario [189]. These changes would increase the relative ice crystal sedimentation rate and can shorten the time required for the ice crystals to encounter sub-saturated air, thereby reducing its contrail lifetime. The shorter contrail lifetime, in turn, reduces the available time for contrails to spread and lowers the contrail coverage area [208], [206]. When taken together, these changes generally lower the contrail climate forcing via two different pathways: (i) the smaller contrail optical depth lowers the local contrail net radiative forcing (RF'), i.e., the change in radiative flux over the contrail area at a given time [178]; and (ii) the smaller contrail lifetime and coverage area lowers the contrail energy forcing, i.e., the cumulative contrail climate forcing throughout its lifetime [209],

$$EF_{contrail}\,[J] = \int_0^T RF'_{net(t)} L_{(t)} W_{(t)}\, dt \tag{6.3}$$

where *L*, *W* and *T* are the contrail length, width, and lifetime respectively.

Table 6.3 summarises the results of the different modelling studies where: (i) five out of the six studies found a 15–60% reduction in the contrail net RF resulting from a 50–80% reduction in the soot EIn; (ii) one study [184] yielded inconclusive results, but the reported values likely represent the contrail net RF' instead of the regional annual mean net RF [143]; and (iii) a sensitivity study found a 60% increase in global contrail net RF resulting from a two-fold increase in soot EIn. While these results imply that decreasing the aircraft particle number emissions could mitigate the contrail climate forcing, further research is required to confirm this benefit. This is because existing contrail modelling studies do not account for the potential activation of vPM in the 'soot- poor' scenario [121], which could underestimate the initial contrail ice crystal number and contrail climate forcing for lean burn powered aircraft and / or low aromatic fuels. Nonetheless, we postulate that this limitation is unlikely to significantly change these findings in the near term because: (i) less than 5% of the global aviation fleet is currently powered by cleaner lean-burn engines that operate in the 'soot-poor' regime [122]; (ii) an increasing fraction of vPM can only be activated when the ambient temperature is significantly below TSAC [160]; and (iii) lowering the FSC may also leads to a reduction in the number and size of vPM [56], both of which could lead to a smaller relative initial contrail ice crystal number. However, much of this is speculative, since the nature of the volatile particle (thought to be chemi-ions, condensable organic species and sulphur-based species) has not been adequately characterised with measurements, and the modelling [160] requires such measurements to confirm or otherwise, this effect. This is a future research requirement.

6.6. Investigating the potential to mitigate aviation's climate impact via the modification of fuel properties

The focus of this section is on compiling data from previous experimental campaigns, particularly those that measured PM emissions from aircraft gas turbines with different fuel properties.

Summary

- The volume of the fuel aromatic content influences various fuel properties. It is negatively correlated with the fuel hydrogen mass content (and its corresponding water vapour emissions index), and the fuel lower calorific value; and is positively correlated with the fuel density.
- There is scientific consensus that the fuel aromatic content is positively correlated with the number, mass, and size of soot particles emitted by aircraft gas turbine engines, whereas the fuel sulphur content is positively associated with the number, mass, and size of volatile particulate matter (vPM) emissions.
- Several studies suggest that the fuel hydrogen mass content and volume of naphthalene content serve as better predictors of fuel sooting tendency than the volume of fuel aromatic content. This is because these variables can better capture the variations in the hydrogen-to-carbon (H/C) ratio between different aromatic compounds.
- Ground-based measurements of soot emitted by rich-quench-lean (RQL) combustors show that

lowering the fuel aromatic content results in a: (i) larger relative reduction in soot number and mass emissions at lower engine thrust settings (i.e., idle and descent conditions); and (ii) smaller relative reduction at high engine thrust settings (i.e., climb out and take-off conditions) owing to differences in the soot formation pathway.

- An assessment of five experimental campaigns that measured the soot emitted by RQL combustors at cruise altitudes found that low- and zero-aromatic fuels reduced the soot particle number emissions by 40%, on average. However, the relative change in volume of fuel aromatic content does not appear to influence the magnitude of reduction in soot emissions, possibly due to increased measurement uncertainties.
- Lowering the volume of fuel aromatic content increases both the fuel water vapour emissions index and lower calorific value. According to the Schmidt-Appleman Criterion, these changes enable contrails to form at higher ambient temperatures (up to 0.5 K) and increase the likelihood of contrail formation.
- In the 'soot-rich' scenario, characterised by an aircraft soot number emissions index (EI_n) exceeding 10^{14} kg^{-1}, both in-situ measurements and contrail models show that reducing the lowering the aircraft soot number emissions reduces the initial contrail ice crystal number, thereby resulting in a larger relative ice crystal size and a smaller relative optical depth in young contrails.
- For persistent contrails that were formed under 'soot-rich' conditions, global and regional contrail modelling studies suggest that lowering the aircraft soot number emissions reduces the contrail optical depth, lifetime, and coverage area, all of which contributes to lowering the contrail climate forcing.
- In the 'soot-poor' scenario where the soot EI_n is below 10^{14} kg^{-1}, parcel model simulations indicate that the initial contrail ice crystal number could be up to three orders of magnitude higher than the soot emissions under temperature conditions below those of threshold formation, due to the activation of vPM and ambient aerosols. However, further research is required because existing global/regional contrail simulations do not currently account for these effects.

6.7. Implications of fuel hydrotreatment

Based on this literature review, this section summarises the potential implications of fuel hydrotreatment in reducing the fuel aromatic and sulphur content, while also assigning a confidence level to each outcome based on the confidence matrix outlined in Table 4b of [58]: [Note, confidence statements below are preliminary and are subject to further discussion and feedback]

1. Lowering the fuel aromatic content is expected to increase the fuel water vapour emissions index and fuel lower calorific value, and when taken together, these effects would increase the likelihood of contrail formation. **(medium confidence**)

2. In the 'soot-rich' scenario where the soot EI_n is $> 10^{14}$ kg^{-1}, lowering the aircraft soot emissions via fuel hydrotreatment is expected to reduce number of ice particles potentially reducing contrail lifetime, coverage area, and contrail cirrus climate forcing. **(low confidence)**

3. Under 'soot-poor' conditions where the soot EI_n is $< 10^{14}$ kg^{-1}, the potential benefits in mitigating the contrail climate forcing via fuel hydrotreatment is uncertain and could be smaller when compared to the 'soot-rich' scenario because vPM and ambient aerosols could activate to form contrail ice crystals. **(very low confidence)**

4. The direct cooling effects of sulphate particles (-7.4 [-19, -2.6] mW m^{-2}) is estimated to be around 8 times larger than the direct warming effects from soot particles (0.94 [0.1, 4.0] mW m^{-2}). Therefore, the reduction of both the soot and sulphate particles via fuel hydrotreatment result in a diminished net cooling effect **(low confidence),** and

5. Soot and sulphate particles can also interact with natural cirrus and lower level clouds, by changing its occurrence and optical thickness, but there is no scientific consensus on the climate forcing resulting from these indirect effects because current estimates vary widely that range between -300 and +13 mW m^{-2}. **(very low confidence)**

6. The uncertainties on the sign and magnitude of any non-CO_2 forcing change combining all non- CO_2 effects of soot and aromatic reductions are currently not known well enough to determine the sign of the potential climate forcing change. Changes in aerosol-cloud interaction from soot and sulphur reduction might counter any potential reduction in the contrail climate forcing. **(very low confidence)**

These implications must be weighed against the potential energy consumption that is required for fuel hydrotreatment. For context, the CO_2 emissions emitted from burning aviation kerosene fuel is estimated to be 3159 kg CO_2 per tonne of fuel, whereas the CO_2 emissions from fuel hydrotreatment is currently estimated to be 97 kg CO_2 per tonne of kerosene which represents an additional 3% of CO_2 emitted from the fuel burned [121]. Finally, to address the risk outlined in Point (3), a potential solution could involve limiting the use of hydrotreated fuel to RQL combustors, as they always operate in the 'soot-rich' scenario, for which the potential contrail climate benefits via lower aircraft particle number emissions are less uncertain. This would add an element of complexity at the airport in terms of fuel storage, distribution and refuelling of aircraft.

6.8. Balancing non-CO_2 effects potentially increased lifecycle emissions of CO_2

Nature of the problem

As outlined above, contrails and contrail cirrus have been estimated to have the largest non-CO_2 forcing, at present, of those terms for which a best estimate is possible. There are preliminary indications from both observations [166] and modelling [175], [210] that ice crystal numbers (N_{ice}) can be reduced for the bulk of the present-day fleet for which soot number emissions are $>10^{14}$ kg_{fuel}^{-1}, by using lower aromatic content fuel. It is assumed that lowering N_{ice} will reduce control for such a case. The case for the soot-poor regime ($<10^{14}$ kg_{fuel}^{-1}) has not yet been observed but modelling indicates that increases in N_{ice} may occur at low temperatures [160], [165]. There is empirical evidence that aromatic species, particularly multi ring aromatics such as di-aromatics are partly (but not wholly) responsible for soot formation [39], [53], [136]. Thus, if these aromatics are reduced, then the working hypothesis is that contrail ERF may ultimately be reduced (see aforementioned caveats). Due to other potential non-CO_2 effects of soot reduction on aerosol cloud interaction, the overall sign of non-CO_2 ERF change remains to uncertain to call. The climate forcing from aviation induced aerosol cloud interaction needs to be a priority research area.

If the hydrotreatment of fuel at the refinery involves extra energy and therefore CO_2 emissions [211], then the question is whether there is a net overall climate benefit. This is by no means a simple question, and aspects of the concept of carbon dioxide equivalent emissions needs to be considered in detail. In the following section, the concept of 'carbon dioxide equivalents' is outlined and the difficulties involved in comparing the effects of long-lived greenhouse gases such as CO_2 with short-lived climate forcers, like contrails.

CO_2 equivalent metrics and their application

Carbon dioxide equivalent metrics (CO_2e) are a means of interchanging the effects of a non-CO_2 climate forcing agent into 'equivalent' CO_2 emissions. The most widely used and well-known CO_2e metric is the Global Warming Potential (GWP) calculated over a particular time horizon (TH). This is essentially the integrated radiative forcing response to (commonly) a pulse release of x kg of a climate forcer over y years divided by the integrated radiative forcing from the same pulse emission of x kg CO_2 over y years. The GWP was originally designed for comparisons of long-lived greenhouse gases, such as nitrous oxide (N_2O), halocarbons and shorter-lived greenhouse gases such as methane (CH_4). The GWP has been used since the early 1990s and updated values published in IPCC assessments. Inherent in the usage of the GWP is the calculation period of 'y' years, the time horizon, and 100 years has been adopted in international and national policy although there is little objective rationale for the choice of one TH over another.

Despite its name, the Global Warming Potential is not necessarily a good proxy for temperature response and an analogous temperature CO_2e metric – the Global Temperature change Potential (GTP) [212] has been devised as an alternative and extends the radiative response of pulse emissions to their temperature effect, via some simplified climate model response. There are other derivative natural science CO_2e metrics such as the GWP "star" (GWP*) [213], the integrated Global Temperature change Potential (iGTP) [27], the Average Temperature Response (ATR) [214] and econometric CO_2e metrics that seek to take a natural science metric a step further to account for monetary valuation over time, e.g., the Global Damage Potential (GDP) [215]. A detailed overview can be found in e.g. [168], [169], [27].

The core issue for aviation non-CO_2 forcers is that they represent "short lived climate forcers" (SLCFs), and their usage in CO_2e metrics is highly debated, since the original metrics of GWP, and other natural science derivative metrics, were envisaged for use with other long-lived greenhouse gases under, e.g., the Kyoto "basket".

In terms of aviation non-CO_2 forcers, the most up to date values for GWP, GTP, GWP* for a range of THs are given by [58]. In the consideration of potentially lowering the aromatic content of fuel to reduce contrails, it is important to account for any increase in energy demand at the refinery to hydrotreat the fuel, and the origin of that energy. If the energy is from fossil fuels, an upstream out of (aviation) sector emission of CO_2 is likely. Thus, it is important to consider whether there is a net climate benefit of potentially reducing contrails, if CO_2 emissions are marginally increased.

Such a comparison is not straightforward because of the extremely long lifetime of CO_2 (approximately 20% of a notional emission remains in the atmosphere for millennia). In order to illustrate this, Figure 6.6 shows contrail CO_2e emissions for 2018 compared with actual tailpipe emissions of CO_2 from [58]. It can be readily seen that the CO_2e emissions vary across the example CO_2e metrics and THs by a factor of approximately 20. All the quantifications shown are 'correct' (uncertainties are not shown), yet a value judgement would be required to select one metric/TH over another in deciding whether there is a 'net climate benefit'.

Moreover, the 'choice issue' is not as straightforward as an examination of Fig. 6.6 would imply, since uncertainties in the underlying ERFs were not propagated forwards to the CO_2e metrics reported by [58]. From Fig. 6.5, it can be seen that the uncertainties for contrails and contrail cirrus are approximately 8x larger than those for the CO_2 forcing; uncertainties on the CO_2e emissions would approximately scale linearly.

Irrespective of choices of emission metric, given known future emission scenarios for soot and carbon dioxide, the future global-mean temperature response can be estimated using ERF estimates and a well-tested climate model emulator (such as FaIR - [216]). This can be on a best estimate basis or including known uncertainties. This will allow the user to gauge, in a quantitative way, where a particular change might make the climate better or worse. Such calculations rely on future emission predictions and an understanding of how use of alternative fuels would scale up over time. To generalise, uncertainties and multiple scenarios would need to be explored. Such an exercise has not yet been undertaken.

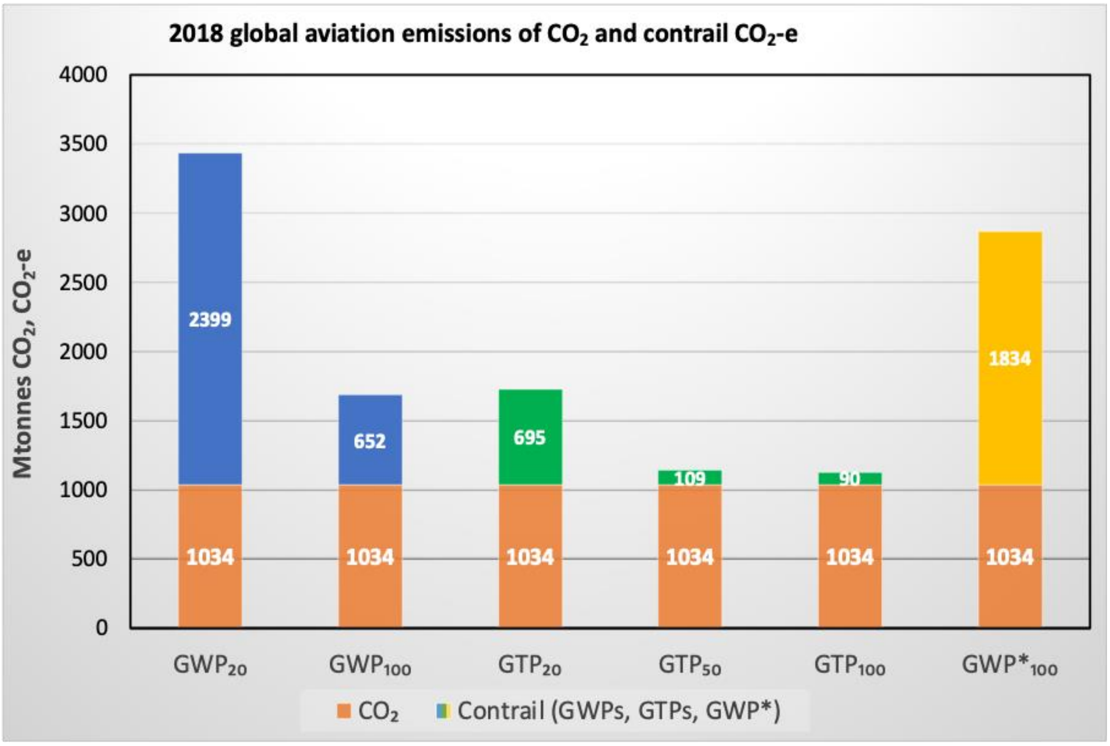


Figure 6.6 Emissions of CO_2 for the 2018 global fleet and CO_2e emissions for contrails for examples of CO_2e metrics and associated time horizons (from [58], [121]).

6.9. Summary

Question 1: “What is the size of the ‘contrail effect’ in terms of effective radiative forcing, the metric commonly used for quantification? What are the associated uncertainties, is the term sufficiently well-characterised and is the science still evolving?

The size of the effect in terms of effective radiative forcing was assessed in a multi-model comparison to be 57 mW m^{-2} (17–98 mW m^{-2} uncertainty range) for 2018 [58]. Air traffic declined over the period of the COVID pandemic dramatically but is estimated to have reached 68.5% of the high of 2019 pre-pandemic levels (IATA, 2023). Assuming linearity between traffic and global contrail ERF, this would imply a 2022 ERF of approximately 41 mW m^{-2} under the same assessment assumptions. The uncertainties remain large and the basis for model evaluation of ERF remains small (3). The ERF/RF adjustment used by [58] remains poorly characterised and is highly uncertain, although there is consensus that it is <1, possibly of the order 0.5. Only one published global climate model with a representation of contrails and contrail cirrus with a self-consistent water-vapour budget is currently in operation and continues to be actively developed (ECHAM climate model, Germany). A recent improvement in the representation of contrail processes reduced the RF calculated by the ECHAM model by 22%. Overall, the evaluation of the size of the contrails and contrail cirrus ERF effect remains of low confidence.

Question 2: "What change in soot emissions and consequential radiative forcing may arise from a reduction in the aromatic content of fossil fuel? How certain is this? What is the evidence base?"

Many measurements at ground level, and a few at cruise altitudes suggest that lower aromatic content fuel reduces soot number concentrations. These results are usually from measurements of bio-derived 'SAF' in current engines, most of which have emissions in the 'soot rich' regime of
$>10^{14}$ soot particles kg^{-1} fuel. However, soot is not reduced to zero, with a zero aromatic content. This suggests that other compounds in the fuel also contribute to soot formation. Subtle changes in ice crystal size distribution and number have been observed from one campaign set of observations, for which SAF was used.

Limited modelling with the ECHAM GCM suggests that for the soot rich regime, the RF may be reduced non-linearly for reductions in soot particles in the exhaust. The parameterizations and assumptions that these global model calculations use are simplified, and not applicable to all types of engine emissions, particularly lean burn. Such reductions in RF from fewer soot particles do not necessarily apply to the 'soot poor' regime, for which ice particle number concentration may *increase* according to poorly-constrained microphysical modelling [160]. As a result, RF may potentially *increase* again at soot levels $<10^{14}$ soot particles kg-1 fuel. There is very low confidence in the evidence for this phenomenon. Overall, there is no simple answer to this question (2): in the soot rich regime, reductions in aromatic content may potentially reduce soot particle numbers and ice crystal numbers, and RF, non-linearly (one model calculation). Lean burn engines already have soot emissions that are orders of magnitude lower than the rich-burn engines, so tens of percent reductions in aromatics are unlikely to make large differences to soot emissions from these engines.

Reductions in aviation soot emissions may reduce the soot aerosol-cloud interaction effect. Currently, this is considered to be a negative ERF from some model calculations (as large as negative 100s of mW m^{-2} [201] - [205]), although others consider the effect to be potentially negligible [204]. No best estimate of ERF, in an assessment sense, is possible at the moment. If the effect is shown to exist, then reduction of aircraft soot would logically reduce this potentially negative forcing. By how much is completely unknown, since no baseline is available, nor have soot reduction scenarios been explored.

Question 3: "What increase in terms of life-cycle emissions of CO_2 might be involved in the extra processing of aviation kerosene at the refinery to reduce aromatic content?

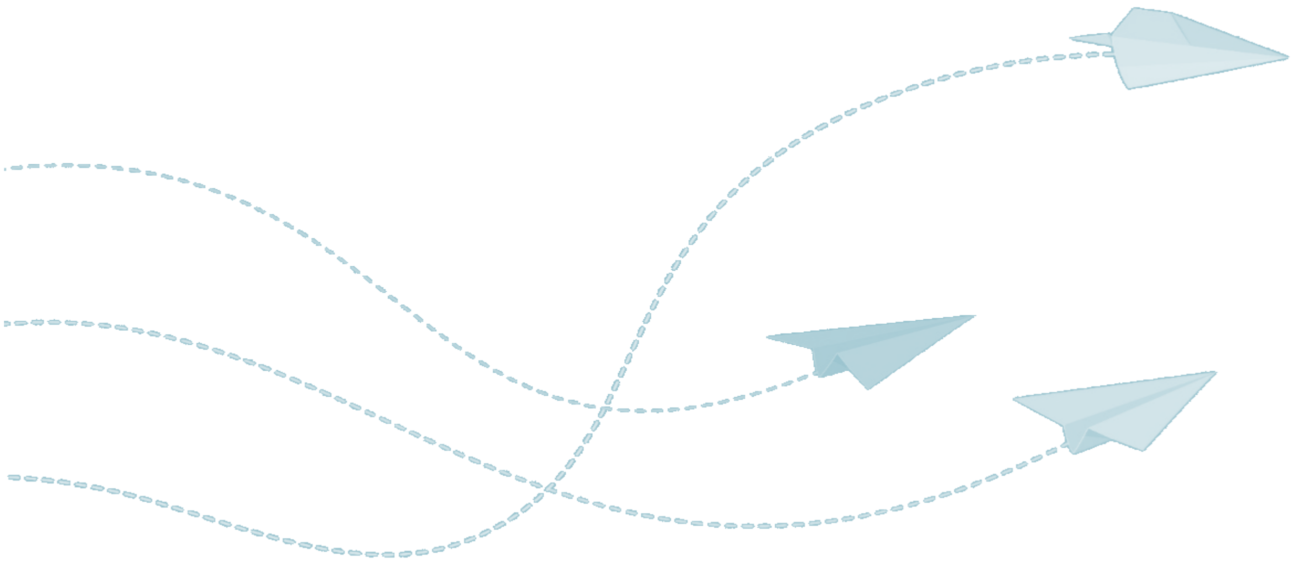
In prior work [211], a Life Cycle Analysis (LCA) emission of 97 kg CO_2, per tonne of aviation fuel was calculated. A tonne of aviation fuel combusted results in 3.16 tonnes of CO_2, therefore an additional 97 kg CO_2 emitted at the refinery represents a 3% increase in LCA CO_2, assuming that non-renewable energy is used to power the refinery.

Question 4: "If an increase in LCA CO_2 is involved, then what equivalency metric could and should be used to balance the potential reduction of the radiative impacts of persistent contrails against increased CO_2 emissions?

There are a number of CO_2e metrics available to convert a short-lived climate forcer to CO_2e emissions.

These include the global warming potential, the global temperature change potential, and the GWP 'star'. Other derivative natural science metrics also exist such as the Average Temperature Response (ATR) and combined pulse/sustained metrics. All of the aforementioned metrics require a specified time-horizon over which the calculation is made, which can strongly affect the result. GWP* is less affected by the time horizon assumed but still requires a prior averaging time, so is not entirely devoid of a time element. This too, can affect the results. Using the metric values for GWP, GTP and GWP* for THs of 20, 50, 100, the additional CO_2e for contrails can range between 0.09 to 2.32 tonnes or a tonne of aviation CO_2. There is no single answer, they are all correct within the constraints of the calculation. The GWP100 for contrail cirrus (the value from Lee et al., [58] is 0.63) is the conventional one used in climate policy but there is large disagreement in the literature over the usage of (unmodified) GWPs to represent short-lived climate forcing agents. Arguably, if one wanted to use temperature as a metric for mitigation, then a GTP may be a better choice. Nonetheless, a TH still has to be specified, which could be e.g. 0.7,
0.1 and 0.09 for 20, 50, and 100 years, respectively (uncertainties in the underlying ERFs are not included). A number of metrics could be used, but which should be used (over others) is indeterminable. However, the degree of benefit of aromatic reduction will be strongly CO_2e metric dependent; the degree of net benefit, when additional CO_2 is considered is also likely to be CO_2-e metric dependent. The uncertainties in the underlying contrail ERF will also strongly affect perception of benefit.

Irrespective of choices of emission metric, given known future emission scenarios for soot and carbon dioxide, the future global-mean temperature response can be estimated using ERF estimates and a well-tested climate model emulator (such as FaIR). This can be on a best estimate basis or including known uncertainties. This will allow the user to gauge, in a quantitative way, where a particular change might make the climate better or worse. Such calculations rely on future emission predictions.



7. Conclusions

7.1. Summary of findings

Aviation affects climate through its CO_2 and non-CO_2 emissions. The Government has committed to delivering greener transport and supporting the missions to kickstart economic growth and to make Britain a clean energy superpower. In 2023, DfT launched a non-CO_2 research programme, alongside NERC, DBT and the ATI to better understand aviation's non-CO_2 impacts and to identify and develop potential mitigation options. Contrails and contrail cirrus are considered to be an important component of aviation's non-CO_2 impacts on climate, and there is evidence that the emissions of soot, thought to largely originate from the aromatic content of fuel, might be limited by reduction of the aromatic content of conventional fossil jet fuel. This present work was commissioned to provide a review and assessment of the literature that has been undertaken to understand the relationship between the aromatic content of jet fuel and contrail formation.

The *Closing the Gap* jet fuel test campaign aimed to investigate the impact of aromatics content on non-CO_2 emissions and fuel performance. The findings of which provide additional technical insights, supporting the long-term goal of investigating reducing aromatics in jet fuel to mitigate non-CO_2 emissions from the aviation sector. By reducing aromatics, the aviation industry can contribute to lowering its overall climate impact beyond CO_2 emissions.

Contrail formation and its effect on radiative forcing of climate has been studied intensively since the publication of the Intergovernmental Panel on Climate Change's Special Report, 'Aviation and the Global Atmosphere'. While much progress has been made in understanding the mechanisms, occurrence and effects of contrails and contrail cirrus, **scientific confidence in the quantification of the global effect of contrails remains 'low' and there are large uncertainties over current estimates**, which are only estimated with two current 'closed budget'[4] models, globally [Chapters 1, 6].

Soot particles (sometimes termed 'non-volatile particulate matter; nvPM) are emitted by aircraft engines and form condensation nuclei on which ice crystals may form [Chapters 1, 5, 6]. **There is an observed relationship, supported by theoretical modelling, between the number of soot particles emitted, and the number of ice crystals**. The number of ice crystals formed, their shape, size all affect their radiative properties**. If there are fewer ice crystals, the radiative effect of contrails and contrail cirrus is calculated to diminish in a non-linear manner**. The evidence for this is limited to a few studies [Chapters 5, 6].

Soot emissions are firmly established from many ground-based measurements to vary with the aromatic content of the fuel. A few high-altitude measurements confirm this. Thus, the hypothesis is that

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[4] *The effect of contrails is not independent of background water vapour, and a closed budget for water vapour needs to be calculated to establish the true size of the effect (the 'effective radiative forcing' – see Chapter 6), which may be less than half the value of the 'radiative forcing' that may be calculated by simply computing the effect of additional notional cirrus-like clouds.*

reducing the aromatic content of the fuel might reduce soot number emissions, with consequential reductions in ice crystal number and radiative forcing [Chapters 2, 5, 6]. Most of these studies have been based on blends of ‘Sustainable Aviation Fuel’, manufactured from biogenic sources, or synthetically produced blend components, and provide a surrogate for what might happen if the aromatic content of conventional fossil jet fuel were to be reduced.

The details of the chemistry of soot formation from aromatic compounds in the fuel remains poorly understood. **Largely by empirical observation, i.e. without supporting mechanistic evidence and understanding, it appears that di-aromatic compounds, such as naphthalene play a significant (but not sole) role in soot formation in aero engines**.

Jet fuel is a highly complex mixture of largely organic compounds that is specified by international standards to broad characteristics that largely relate to its combustion and safety of usage. For example, the total aromatic content of jet fuel has a maximum and minimum percentage volume for semi synthetic jet fuel (<28%; >8%) but **the detailed components of the aromatic compounds are not routinely measured and may vary with crude oil type, refinery processing, and between batches**. The aromatic content of jet fuel is naturally present in fossil fuels, and while it has lower energy density (per unit mass) than other jet fuel components, it has positive uses in aircraft engines and systems in terms of providing lubricity and maintaining the integrity of fuel systems by the swelling of elastomeric seals in fuel systems. **If the aromatic content of jet fuel were subject to more stringent limits, this would require further investment at refineries and in testing facilities, particularly if individual compounds, such as naphthalene, were to be targeted**. A hydrocracker unit might cost £1-2 billion depending on the size while a kerosene hydrotreater (Kero HT) unit is normally 1/3-1/2 of that cost.

It has been suggested that the relative hydrogen content of fuels could represent a ‘proxy’ for regulating aromatic content. **While there is a good body of evidence of an inverse correlation between hydrogen content and aromatic content, there is a large degree of scatter in the available data, and such an approach may represent a ‘blunt instrument’ for regulation of very specific compounds within aromatics that result in soot particles**. Such an approach would carry a significant risk of being ineffective and essentially be based on poor evidence that the outcome would be as desired [Chapter 3].

Limiting aromatic content of jet fuel will require additional processing of fuels at the refineries, largely through hydrotreating or hydrocracking. **This will increase costs, require an increased supply of hydrogen and utilise extra energy with resultant extra CO_2 emissions** [Chapters 4, 6]. This could also result in a conflicting demand for hydrogen, which is required for the production of synthetic blend components, SAFs and for use in hydrogen-powered aircraft [Chapter 3] and ultimately limit the potential for blending between SAF and conventional fuels with in the permitted 8% aromatic limit for blended Jet A-1/A.

Because of the safety implications, should any changes to jet fuel specification be made, a careful and comprehensive risk analysis would need to be undertaken relating to ground handling of fuel, airframe and engine performance [Chapter 4].

Since extra CO_2 will be likely emitted over a counterfactual for the hydrotreatment/hydrocracking of fossil jet fuel to reduce aromatic content from the production of hydrogen and extra energy requirements at the refinery, this needs to be carefully assessed. At present, only two independent studies are available of this, but they are in good agreement, **suggesting that an extra 3% CO_2 would be emitted, for every tonne of jet fuel produced, as a result of these associated industrial processes** [Chapters 4, 6].

The comparison of the potential reduction in the warming effect of contrails over the warming effect of additional CO_2 emitted in the production process of aromatic-reduced jet fuel is by no means a simple or straightforward calculation [Chapter 6]. This is because of the vastly different timescales of the warming effects of contrails and CO_2, such that subjective choices of timeframes need to be considered. We show that depending on timescales and metric choice (CO_2 emission equivalence metric; CO_2e), it is possible to demonstrate that the CO_2e of contrails is either 2.3 times larger than a tonne of CO_2 or around 10% of a tonne of CO_2. This needs to be studied in detail, since there are no studies of this particular aspect available.

In summary, until many of the uncertainties outlined in this report are addressed on safety, feasibility, cost, and environmental integrity, potential reduction of the aromatic content of jet fuel has large risks of being costly and ineffective, potentially even having an inadvertent adverse climate outcome.

7.2. Summary of recommendations

1. Improve the evidence base to better understand whether adopting regulatory actions to target soot's role in contrail and contrail cirrus formation would be an effective measure to mitigate aviation's non-CO_2 effects on climate.

This requires large scale international research efforts, as reflected by e.g. announcements of the UK Government's multi-year non-CO_2 Research Programme delivered by NERC, and ATI, and EU-H2020 initiatives to research the non-CO_2 effects of aviation, and in particular, contrails. In-flight measurements still have a considerable level of uncertainty and do not show a clear relationship between aromatic levels and soot emissions. This requires further investigation. Reductions in aviation soot emissions may reduce the soot aerosol- cloud interaction effect. Currently, this is considered to be a negative Effective Radiative Forcing (ERF) from some model calculations (as large as negative 100s of mW m^{-2}), although some studies consider the effect to be potentially negligible. No best estimate of ERF, in an assessment sense, is possible at the moment. If the effect is shown to exist, then reduction of aircraft soot would logically reduce this potentially negative forcing. By how much is completely unknown, since no baseline is available, nor have soot reduction scenarios been explored.

2. Undertake a detailed study (within the existing known uncertainties) of the potential trade- offs between decreased contrails and contrail cirrus by reducing soot emissions compared to increased CO_2 emissions at the refinery.

This will require modelling of additional energy costs at the refinery and exploration of different CO_2-e metrics. This is important since without such a detailed study, there is a significant risk that the environmental outcome is worse than the counterfactual of no regulation. Such a study could be initiated within the UK's academic scientific capability and requires inputs from atmospheric science, fuels and emission technology.

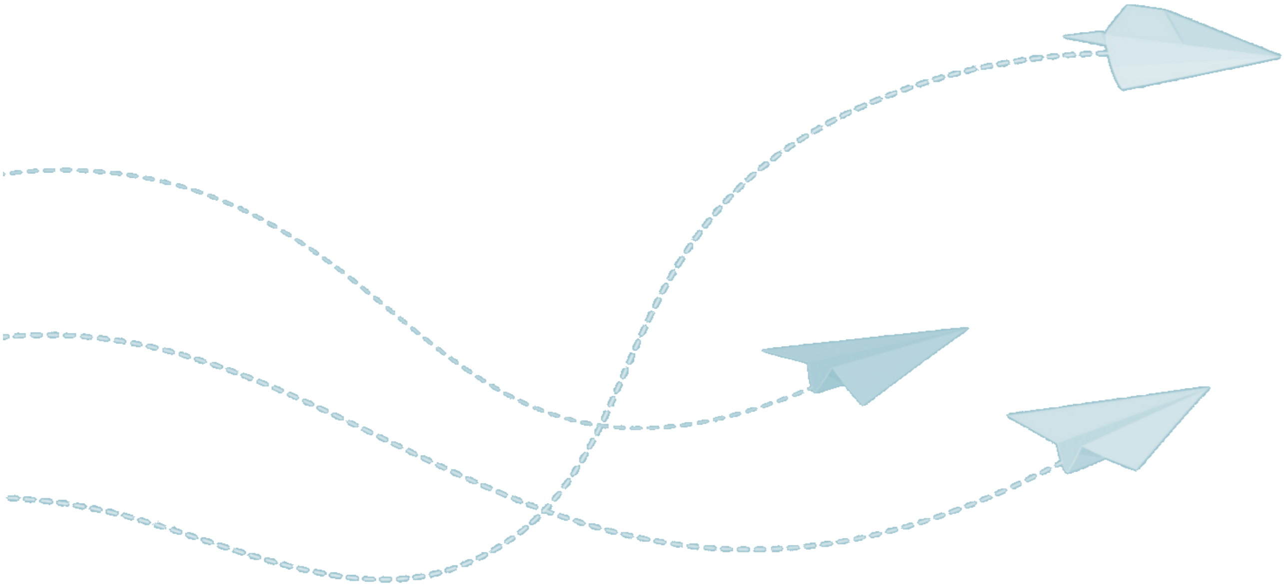
3. Undertake a detailed study of the trade-offs in fuel properties as the aromatic content changes and its viability to be used in aviation.

Studies where one fuel has been hydrotreated to different levels to observe the changes in fuel properties are limited (there are only 3) and only at a pilot plant scale. This is important to assess the extent to which other critical fuel properties are changed by reducing the aromatic content.

Such a study would need to test a small number of representative fuels to then extrapolate the impact on a whole sector, which could be challenging, although it does allow any study to be targeted specifically to investigate properties such as lubricity and thermal stability along with elastomer and soot creation performance.

This would require the use of pilot scale capabilities to produce relatively small volumes of fuel (of the order of 200L) from varying levels of hydrotreatment from a representative number of crude sources. A limited number of facilities to produce this level of product exist in Europe, namely Air BP's site in Bochum, Germany.

Further work at the range of technology readiness levels (TRLs) and across all aero engines by original equipment manufacturers (OEMs) would be necessary with low aromatic products to guarantee safe, reliable and cost-effective flight for passengers and operators.



Appendix A: brief description of aromatic measurement test methods

ASTM D1319 test method for hydrocarbon types in liquid petroleum products by Fluorescent Indicator adsorption (FIA) [5]

This is the oldest (and original) method for measuring aromatics in jet fuels and is still in use (see later). It is also the only method that is considered as a manual method in that all others are instrumental. In summary, a small fuel sample (<1 ml) is introduced into a glass adsorption column packed with activated silica gel. A layer of silica gel containing a mixture of fluorescent dyes is also present. The sample is first adsorbed on the gel, alcohol is then used to desorb the sample down the column. The hydrocarbons are separated in accordance with their adsorption affinities into aromatics, olefins, and saturates along with the fluorescent dyes. The hydrocarbon types, as the aromatic, olefin, and saturate show in zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.

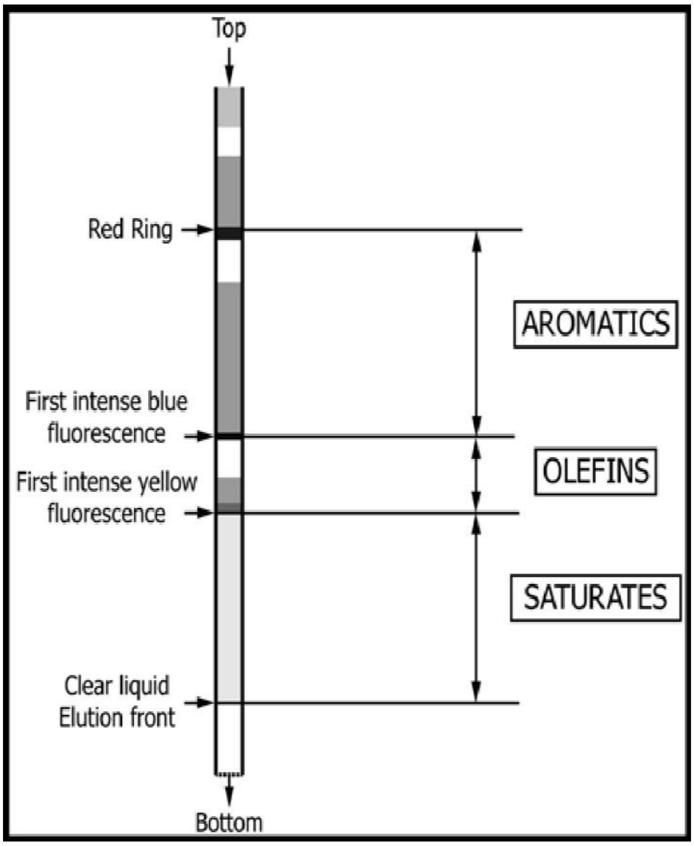


Figure A.1: Example of an FIA visualisation (ASTM D1319)

From the description it is clear that this method only provides a single number for the classes of aromatics (single and multi-ring), olefins which in good quality fuels is virtually zero and remainder being saturated paraffins. Since this method counts all aromatic types it is usually used in conjunction with ASTM D1840 to measure multi-ring aromatics expressed as naphthalenes.

ASTM D1840 test method for naphthalene hydrocarbons in aviation turbine fuels by ultraviolet spectrophotometry [6]

The total concentration of naphthalenes in jet fuels is determined by measurement of the absorbance at 285 nm of a solution of the fuel at known concentration. The spectrometer used (sensitivity, path length and slit width etc), the cells and the dilution of sample to get the absorbance in the correct range are all defined. The absorbance is measures and the percentage of multi-ring aromatics mass/mass is expressed as naphthalenes.

Notes:

Fuels contain a range of multi-ring aromatics, but the method does not have capability to separate them out so provides just a single number expressed as "naphthalene" percentage by mass. Although the method has been in use for many years and is adequate for specification testing on typical conventional jet fuels there is a significant assumption regarding the absorption of compounds being measured.

Therefore, instead of direct calibration of the spectrophotometer with known multi-ring aromatics or pure naphthalene, the average absorptivity of the C10 to C13 naphthalenes at 285 nm is be taken at 33.7 L⁄g·cm. The data used to calculate this average are cited and has been accepted by the industry as a good compromise.

Most specifications do not require naphthalenes to be carried on every batch. It is only applied when the smoke point is below 25 mm when the test is required (see Test Method Applications).

ASTM D2425 test method for hydrocarbon types in middle distillates by mass [218]

This test method uses a mass spectrometer to determine the hydrocarbon types present in conventional and synthesised hydrocarbons. Samples with average carbon number value of paraffins between C12 and C16 and containing paraffins from C10 and C18 can be analysed. Eleven hydrocarbon types are determined. These include: paraffins, non-condensed cycloparaffins, condensed dicycloparaffins, condensed tricycloparaffins, alkylbenzenes, indans or tetralins, or both, CnH_2n-10 (indenes, etc.), naphthalenes, CnH_2n-14 (acenaphthenes, etc.), CnH_2n-16 (acenaphthylenes, etc.), and tricyclic aromatics. Results are quoted for each class (See table A.1) in concentration percentage by mass.

Samples are separated into saturate and aromatic fractions by liquid chromatography, and each fraction is analysed by mass spectrometry. The analysis is based on the summation of characteristic mass fragments to determine the concentration of hydrocarbon types.

Table A.1: Breakdown of species by ASTM D2425

SaturateFraction:
Paraffins
Monocycloparaffins
Dicycloparaffins
Tricycloparaffins
Alkylbenzenes
AromaticFraction:
Paraffins
Cycloparaffins
Alkylbenzenes
Indanand/ortetralins
CnH$_2$n-10
Naphthalenes
CnH$_2$n-14
CnH$_2$n-16
CnH$_2$n-18

Notes:

Given the wide range of molecules even within a given fraction there has to be some assumptions/simplification to reduce the data. Therefore, mole fractions are calculated based on the average C number. This is achieved as follows:

The average carbon numbers of the hydrocarbon types are estimated from spectral data. Calculations are made from calibration data dependent upon the average carbon number of the hydrocarbon types. The results of each fraction are mathematically combined according to their mass fractions as determined by the separation procedure. Results are expressed in mass percent.
It has been noted in industry discussions that this method is not easy and has some limitations and is not in common use. Therefore, like some other methods, it is being superseded by 2DGC.

ASTM D6379 test method for determination of aromatic hydrocarbon types in aviation fuels and petroleum distillates—high performance liquid chromatography method with refractive index detection [219]

This test method is based on high performance liquid chromatography with a set of polar columns and determines monoaromatic (MAH) and di-aromatic (DAH) hydrocarbon contents in aviation kerosenes. The total aromatic content is calculated from the sum of the individual aromatic hydrocarbon-types. These columns have very low affinity for the non-aromatic hydrocarbons and exhibit a pronounced selectivity for aromatic hydrocarbons. As a result of this selectivity, the aromatic hydrocarbons are separated from the non-aromatic hydrocarbons into distinct bands in accordance with their ring structure. Detection is by refractive index detector that detects the components as they elute from the column. The detector output is continually monitored by a data processor. The amplitudes of the signals (peak areas) from the sample aromatics are compared with those obtained from previously run calibration standards in order to calculate the percent m/m MAHs and DAHs in the sample.

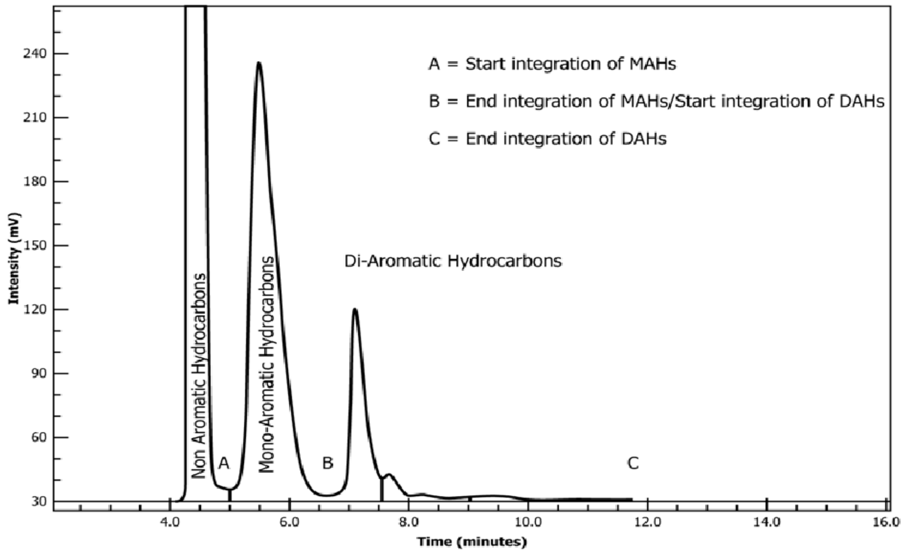


Figure A.2: Output of ASTM D6379

The sum of all the aromatics is reported as the total aromatic content (percent m/m) of the sample. Although this method generates results in m/m, results can also be quoted in percent v/v either by calibrating in v/v or by converting m/m to v/v by using the densities of the sample and standards.

The method reports mono-aromatic, di-aromatic and total aromatic hydrocarbon contents by mass percent.

Notes:

This method was developed over several years to first replace ASTM D1319 (total aromatics) and then later to include replacement for ASTM D1840 (naphthalenes).

Note that due to a residual bias (ASTM D6379 reading slightly higher than D1319) for total aromatics maximum limits are cited as 25% for D1319 but 26.5 for D6379. (See test method applications).

ASTM D8305 test method for the determination of total aromatic hydrocarbons and total polynuclear aromatic hydrocarbons in aviation turbine fuels and other kerosene range fuels by supercritical fluid chromatography [220]

This test method is the determination of the concentration of total aromatics, and total polynuclear aromatic hydrocarbons in aviation turbine fuels and other kerosenes by supercritical fluid chromatography. The method may also be used for the analyses of jet fuels, such as Synthetic Paraffinic Kerosenes (SPK) that contain not less than 0.29 % total aromatics by Test Method D2425.

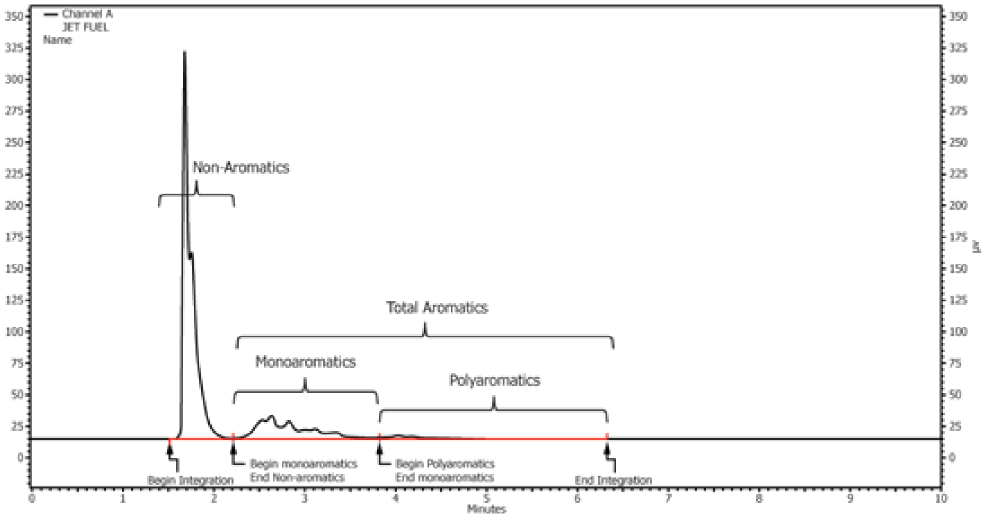


Figure A.3: Typical output of ASTM D8305

The fuel sample is injected onto a packed silica adsorption column and eluted using supercritical carbon dioxide mobile phase. Mononuclear and polynuclear aromatics in the sample are separated from nonaromatic hydrocarbons and detected using a flame ionisation detector. The detector response to hydrocarbons is recorded throughout the analysis time. The chromatographic areas corresponding to the monoaromatic, polynuclear aromatic, and nonaromatic components are determined and the mass percent content of each of these groups in the fuel is calculated by area normalisation.

Notes:

This test method includes correlations t/correction to test methods Test Method D1319 for total aromatics and to Test Method D1840 for total naphthalenes content so results can be calculated to give the same results as D1319 and D1840.

ASTM D8267 test method for determination of total aromatic, monoaromatic and di-aromatic content of aviation turbine fuels using gas chromatography with vacuum ultraviolet absorption spectroscopy detection [221]

This relatively new test method determines total aromatic, monoaromatic and di-aromatic content in aviation turbine fuels using gas chromatography and vacuum ultraviolet detection (GC- VUV). Concentrations of compound classes and certain individual compounds are determined by percent mass or percent volume.

Individual hydrocarbon components are not reported by this test method; however, any individual component determinations are included in the appropriate summation of the total aromatic, monoaromatic or di-aromatic groups. Individual compound peaks are typically not baseline separated by the procedure described in this test method, that is, some components will coelute. The co-elutions are resolved at the detector using VUV absorbance spectra and deconvolution algorithms.

Fuel samples are introduced to a gas chromatographic (GC) system. After volatilization, the effluent is introduced onto a GC column for separation, and then detected by a vacuum ultraviolet absorption spectroscopy detector, separation is accomplished using a 30 m, nonpolar phase capillary column and a moderately fast temperature ramp. Co-elutions are resolved by the detector using vacuum ultraviolet absorbance spectra and deconvolution.

The calculation of the results is based on the determination of the total response areas of each of the classes of saturated, aromatic and di-aromatic compounds. The saturates class includes the summation of the paraffins, isoparaffins, and cycloparaffins (naphthenes). The total aromatics class includes the summation of monoaromatics and di-aromatics (naphthalenes).

The volume percent concentrations (normally quoted) are calculated from the mass concentrations by applying specific component or class-based (typical) density values as appropriate.

UDRI method FC-M-101 flow modulation GCxGC for hydrocarbon type analysis of conventional and alternative aviation fuels [7]

2DGC also known as GCxGC has the capability to identify almost every compound in a jet fuel or blendstock and provide comprehensive information regarding the presence and concentration of all hydrocarbons within the sample.

This method will be used to analyse an organic sample in a complete or “comprehensive” way (every compound is counted) by categorising every component in the mixture as to its compound class using GCxGC and quantifying these categories using FID detection.

In the method a sample is injected into a split injection system and a series of two chromatographic columns (primary and secondary). In this method, the primary column stationary phase is non-polar and the secondary column stationary phase is polar. Between the primary and secondary column a modulation system collects effluent from the first column and introduces it to the second column. In this application, the first column separates the introduced mixture according to the vapour pressure of each component (equates to carbon number) and the second column is a polar column which performs a high speed separation of a portion of the effluent from the first column, based on polarity. Detection is primarily by FID but other technologies may be used alongside FID to enhance detection and speciation including Mass Spectrometry (MS), such as a quadrupole mass spectrometer, or a Time of Flight Mass Spectrometer (TOFMS).

Each component in the mixture will have a unique primary retention time (x-axis) and a unique secondary retention time (y-axis) which allows identification at a very granular level. The secondary column typically terminates in a detector which responds quantitatively to each component. By combining these two chromatographic outputs into a two-dimensional graphical output, it is possible to characterise the entire sample, separated by both vapour pressure (volatility) and polarity. Because components are separated by their chemical compound types, boundaries of each category of chemical compounds can be drawn and applied to each graphical output. Once identified, these templates can be used to consistently measure the compound classes in each GCxGC analysis. The responses are provided in mass and volume % using density information for each of the compound types and the total response is normalised to 100%.

Note that the method defines not only the actual measurement method but critically the way the data needs to be processed to get the output in graphical or tabular form that is to a known standard.

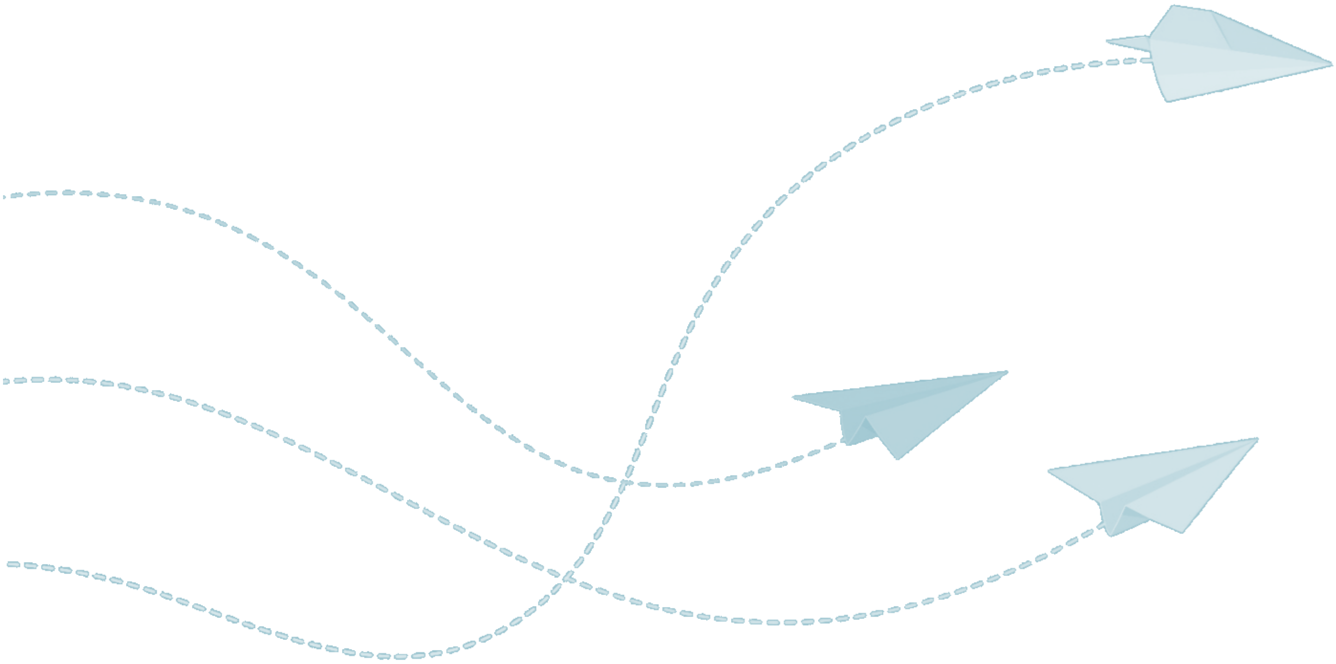
Results can be presented as a Table of compounds and their concentration (See Table A.2 as an example) or as a graphical representation. Typically, "heat maps" are used to show overall composition but more useful are histograms of classes of molecules and their relative concentration, normally with carbon number on the x-axis.

As powerful as the 2DGC methods are it has to be noted that they still cannot fully resolve all the molecules in jet fuels. Specifically, 2DGC cannot resolve isomers of the same basic molecule in terms of branching location etc for either linear (paraffinic) or cyclic (cyclo-parafins or aromatics) and their respective branching of linear attachments. This was illustrated in a study by Joshua Heyne et al [46] which examined these shortfalls in isomer resolution when using 2DGC for prediction of properties for prescreening work but note that work is ongoing to address this issue.

Table A.2 Example of hydrocarbon types by 2DGC [7]

Alkylbenzenes	**n-Paraffins**	**Tricycloparaffins**
benzene (C06)	n-C07 & lower	C10-tricycloparaffins
toluene (C07)	n-C08	C11-tricycloparaffins
C2-benzene (C08)	n-C09	C12-tricycloparaffins
C3-benzene (C09)	n-C10	
C4-benzene (C10)	n-C11	
C5-benzene (C11)	n-C12	
C6-benzene (C12)	n-C13	
C7-benzene (C13)	n-C14	**Summarised categories**
C8-benzene (C14)	n-C15	
C9-benzene (C15)	n-C16	Total Alkylbenzenes
C10+-benzene (C16+)	n-C17	Total Di-aromatics
Di-aromatics	n-C18	Total Cycloaromatics
di-aromatic-C10	n-C19	Total Aromatics
di-aromatic-C11	n-C20	
di-aromatic-C12	n-C21	Total Isoparaffins
di-aromatic-C13	n-C22	Total normal-paraffins
di-aromatic-C14+	n-C23	Total monocycloparaffins
Cycloaromatics	**Monocycloparaffins**	Total dicycloparaffins
cycloaromatic-C09	C07 & lower monocycloparaffins	Total tricycloparaffins
cycloaromatic-C10	C08-monocycloparaffins	Total cycloparaffins
cycloaromatic-C11	C09-monocycloparaffins	Total paraffins
cycloaromatic-C12	C10-monocycloparaffins	
cycloaromatic-C13	C11-monocycloparaffins	
cycloaromatic-C14	C12-monocycloparaffins	
cycloaromatics-C15+	C13-monocycloparaffins	
iso-Paraffins	C14-monocycloparaffins	
C07 & lower	C15-monocycloparaffins	
C08-isoparaffins	C16-monocycloparaffins	
C09-isoparaffins	C17-monocycloparaffins	
C10-isoparaffins	C18-monocycloparaffins	
C11-isoparaffins	C19+-monocycloparaffins	
C12-isoparaffins	**Dicycloparaffins**	
C13-isoparaffins	C08-dicycloparaffins	
C14-isoparaffins	C09-dicycloparaffins	
C15-isoparaffins	C10-dicycloparaffins	
C16-isoparaffins	C11-dicycloparaffins	
C17-isoparaffins	C12-dicycloparaffins	

C18-isoparaffins	C13-dicycloparaffins	
C19-isoparaffins	C14-dicycloparaffins	
C20-isoparaffins	C15-dicycloparaffins	
C21-isoparaffins	C16-dicycloparaffins	
C22-isoparaffins	C17+-dicycloparaffins	
C23-isoparaffins		
C24-isoparaffins		



Appendix B: supporting information for Chapter 3 – fuel production

Example of change in composition as a result of varying levels of hydrotreatment / hydrocracking

In common with other studies [28], [29], Figure B.1 shows clearly the effect of increasingly severe hydrotreatment, firstly removing the di-aromatic (Naphthalene) components and converting them primarily to cycloparaffins and iso-paraffins, which show the largest rise in mass fraction.

As the severity of the hydrotreatment increases, the levels of monoaromatics, particularly around the C8 to C12 range drops significantly compared to the base fuel. Of particular interest is the final hydrotreating step HT-3, which reduces the average HD to below the minimum estimated for the range of conventional fuels in the CRC fuels survey and is likely to be beyond the normal level of hydrotreating observed in commercial fuel production at the current time.

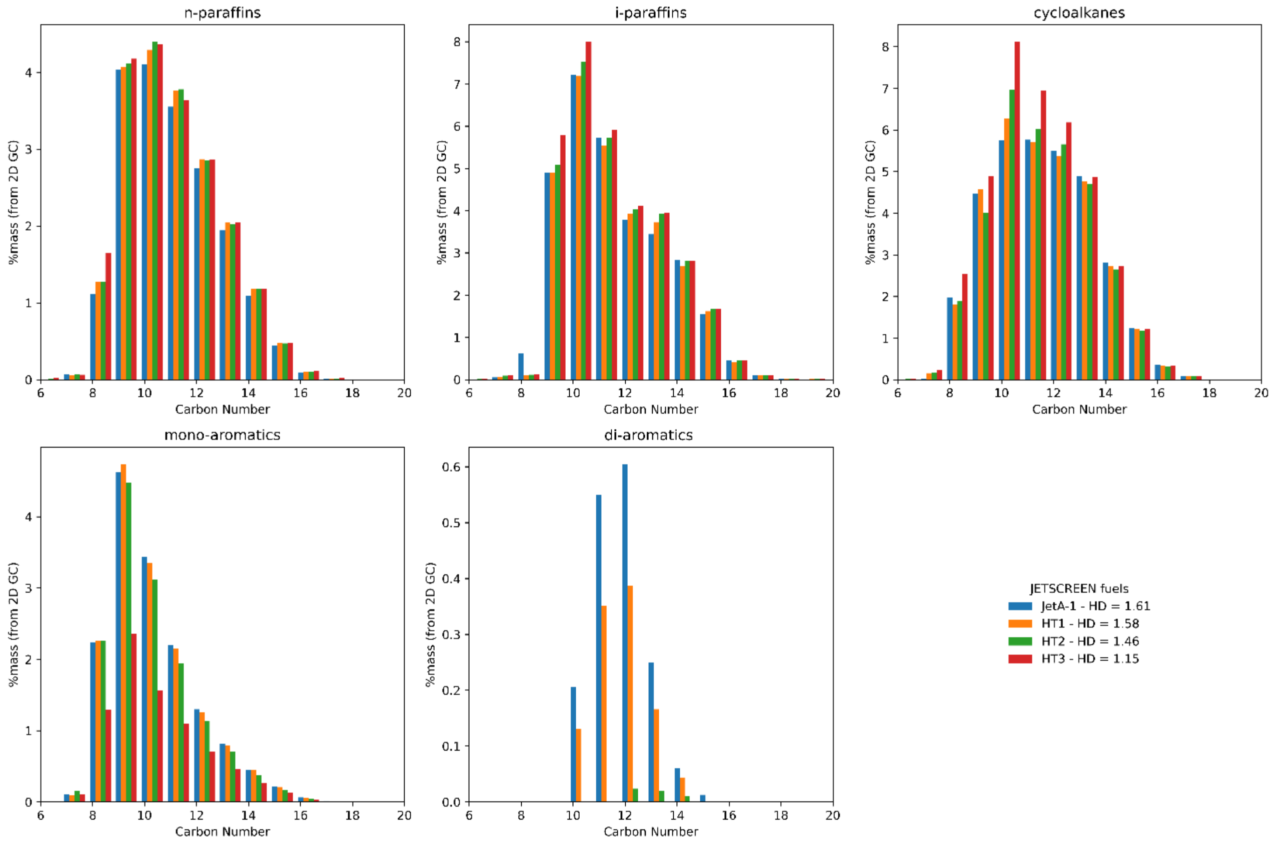


Figure B.1: Change in fuel hydrocarbon speciation through successively severe hydrotreatment (HT-1 through to -3) by molecular class (data source: JETSCREEN project [11])

Appendix C: Supporting information for Chapter 5 – Combustion

Overview of research into soot formation mechanisms

Fig C.1 shows a comprehensive overview of the growth mechanisms of PAHs that have been studied experimentally and theoretically so far. All these mechanisms are based on the "bottom- up" approach, which assumes that PAHs grow from smaller molecules. However, there is also evidence for the "top-down" approach, which involves the fragmentation of larger carbon structures into PAHs. This can happen in thermal treatment of soot particles [222]. Three main types of PAH growth mechanisms have been identified in the last four decades: (i) acetylene additions, (ii) vinylacetylene additions, and (iii) radical reactions. In this section the impact of jet fuel aromatic components on PAH growth mechanism will be studied.

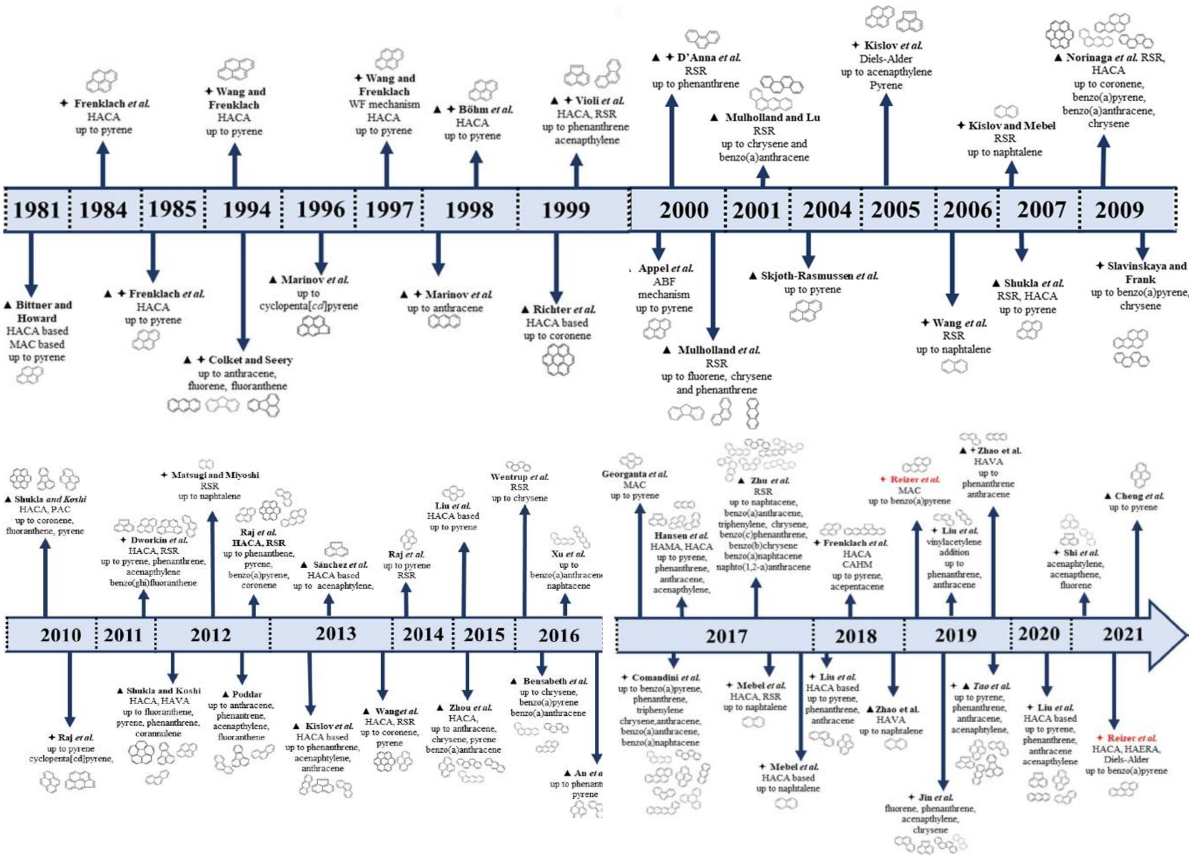


Figure C.1: Review of PAH formation mechanisms studied up to 2022 [97]

Fuel property and test campaign summary tables

Table C.1. Fuel properties form the work of bulzan et al.[112], fuels also used in [113], source provides further detail regarding hydrocarbon source

TEST	**JP-8**	**FT-1 (Shell GTL) [1]**	**FT-1 JP-8 Blend (50/50)**	**FT-2 (Sasol CTL) [1]**	**FT-2 JP-8 Blend (50/50)**
Sulphur (ppm)	1148	19	699	22	658
Aromatics(% vol)	18.6	0	8	0.6	9.1
Distillation,°C					
IBP	158	157	156	160	158
10%	176	162	166	167	170
20%	184	164	170	170	175
50%	207	170	183	180	190
90%	248	186	232	208	233
EP	273	206	264	231	263
Residue,(%vol)	0.8	0.9	1	1	0.8
Loss,(% vol)	0.8	0.9	1	0.9	0.9
Flash Point,°C	46	41	43	42	46
API Gravity	41.9	60.2	50.5	54	47.9
Freezing Point,°C	-50	-54	-60	<-80	-60
Viscosity,mm^2/s	4.7	2.6	3.3	3.6	4.1
Cetane Index	41	58	46	51	45
H Content (% mass)	13.8	15.5	14.5	15.1	14.3
Napthalenes (% vol)	1.8	0	0.8	0	0.8
Heat of Combustion (MJ/kg)	43.3	44.4	43.8	44.1	43.8
Olefins (% vol)	0.9	0	0.6	3.8	3.3
Fuel Ratio (H/C)	1.88	2.19	2.02	2.12	1.99
Specific Gravity	0.816	0.738	0.777	0.768	0.789

Table C.2: Summary of the fuel used in prior experimental campaigns to investigate the fuel property effects on the non-CO_2 pollutants emitted by aircraft gas turbine engines.

Experimental Campaign	Fuel	Fuel properties						
		Aromatics (% vol)	**Naphthalene (% vol)**	**Hydrogen (% mass)**	**Sulphur content (ppm)**	**LCV (MJ kg^{-1})**	**H/C ratio**	**Density (kg m^{-3})**
NASA APEX [118]	JP-8	17.6	0.93	13.69	383	43.22	N/A	819.9
	JP-8 + Sulphur	17.3	1.31	13.67	1595	43.33	N/A	819.4
	Jet-A (High Aromatics)	21.8	1.34	13.7	530	43.27	N/A	811.4
Corporan et al. [223]	JP-8a	19.1	1.5	13.9	800	43.09	N/A	813
	JP-8b	19.0	1.4	13.6	800	43.09	N/A	813
	50% JP-8b + 50% HRJ	9.5	0.70	14.4	500	43.60	N/A	786
	50% JP-8a + 25% HRJ + 25% FT	10.6	0.75	14.4	500	43.50	N/A	786
Timko et al. [114]	JP-8	19	N/A	14	1230	43.1	1.88	N/A
	50% JP-8 + 50% FT	9.5	N/A	14.8	650	43.6	1.95	N/A
	100% FT	0.2	N/A	15.6	30	44.1	2.02	N/A
Timko et al. [224]	Jet A	15.4	2.2	13.9	N/A	43.302	1.92	803
	Jet A-1	18.5	< 0.5	13.9	N/A	43.3	1.92	797
	20% FAME + 80% Jet A-1	14.8	< 0.5	13.5	N/A	42	N/A	808
	40% FAME + 60% Jet A-1	11.1	< 0.5	13.1	N/A	40.3	N/A	825
	50% FT + 50% Jet A-1	9.3	< 0.5	14.7	N/A	43.6	2.04	776
Corporan et al. [225]	100% FT	0	< 0.5	15.4	N/A	44.1	2.17	755
	50% JP-8 + 50% FT (Syntroleum)	8.6	N/A	14.6	420	43.55	N/A	N/A
	50% JP-8 + 50% FT (Shell)	8.6	N/A	14.75	320	43.55	N/A	N/A
	50% JP-8 + 25% HEFA + 25% FT	8.7	N/A	14.55	330	43.55	N/A	N/A
NASA AAFEX-I [53]	JP-8	21.8	1.6	13.6	1148	N/A	N/A	N/A
	FT1 (gas)	0	0	15.5	19	N/A	N/A	N/A
	FT2 (coal)	0.6	0	15.1	22	N/A	N/A	N/A
	50% JP-8 + 50% FT1	8	0.8	14.5	699	N/A	N/A	N/A
	50% JP-8 + 50% FT2	9.1	0.8	14.3	658	N/A	N/A	N/A
NASA AAFEX-II [53]	JP-8	21.8	1.3	13.5	188	N/A	N/A	N/A
	HEFA (tallow)	0.4	0	15.3	6	N/A	N/A	N/A
	50% JP-8 + 50% HEFA	10.2	0.65	14.4	276	N/A	N/A	N/A
	FT	1.4	0	15	4	N/A	N/A	N/A
	FT + sulphur	2.1	0	18.3	1083	N/A	N/A	N/A
NASA ACCESS-I [53]	JP-8	16	1.4	13.9	800	N/A	N/A	N/A
	HEFA (Camelina)	0	0	N/A	0.05	N/A	N/A	N/A
	50% JP-8 + 50% HEFA	8	0.9	14.4	500	N/A	N/A	N/A
A-PRIDE [136]	Jet A-1	17.83	0.78	14.3	N/A	N/A	N/A	N/A
	Jet A-1 + Solvesso 150	21.225	1.0075	13.99	N/A	N/A	N/A	N/A
	Jet A-1 + Solvesso 150	22.025	1.0875	13.9	N/A	N/A	N/A	N/A
	Jet A-1 + Solvesso 150	23.48	1.172	13.8	N/A	N/A	N/A	N/A
	Jet A-1 + Solvesso 150 ND	21.075	0.795	14.1	N/A	N/A	N/A	N/A
	Jet A-1 + Solvesso 150 ND	22.5	0.78	14	N/A	N/A	N/A	N/A
	Jet A-1 + Solvesso 150 ND	23.55	0.775	13.9	N/A	N/A	N/A	N/A
Lobo et al. [126]	Jet A	20	0.8	13.7	200	43	1.89	813
	Sasol IPK	1	0	15.4	14	43.9	2.17	760
NASA ACCESS-II [226]	Medium sulphur Jet-A	21.1	0.68	13.6	416	43.14	N/A	809.2
	Low sulphur Jet-A	21.4	0.68	13.8	22	43.15	N/A	810
	50:50 HEFA:low sulphur Jet-A blend	12.9	0.4	14.7	11	43.52	N/A	787.4
ECLIF I [52]	Ref1: Jet A-1 (Merox)	18	N/A	14.1	1170	42.8	1.922	812.7
	Ref2: Jet A-1 (Bitumen Run)	17.2	N/A	14.1	1350	43.2	1.925	808.9
	SSJF1: 59% Ref1 + 41% SPK	11.4	N/A	N/A	570	43.496	2.029	790.2
	SSJF2: 55% Ref2 + 45% SPK	10.9	N/A	14.7	700	43.54	2.045	783.4
	SSJF3: 86% Ref1 + 14% SPK	15.3	N/A	14.2	1590	43.301	1.954	803.2
	100% FSJF	8.9	N/A	14.5	10	43.33	1.981	807.9
CAAFCEB [227]	Jet A-1	18.5	N/A	13.85	500	N/A	N/A	N/A
	JP-5	20.1	N/A	13.52	200	N/A	N/A	N/A
	ATJ-SPK blend	8	N/A	14.91	0	N/A	N/A	N/A
	ATJ-SPK neat	0	N/A	15.33	0.96	N/A	N/A	N/A
EMPAIREX [140]	Jet A-1	18.1	0.79	13.57	490	43.3	1.88	795.4
	32% HEFA-SPK + 68% Jet A-1	11.3	0.53	14.05	350	43.6	1.95	781.8
ECLIF II [119], [166]	Ref1: Jet A-1 (Merox)	18.8	1.51	13.67	1170	42.8	1.89	N/A
	Ref2: Jet A-1 (Bitumen Run)	17.2	1.83	13.73	1350	43.2	1.9	N/A
	Ref3: Jet A-1	18.6	1.17	13.65	120	43.14	1.88	814.4
	Ref4: Jet A-1	16.5	0.13	14.08	10	43.34	1.95	790.5
	SSF1: 59% Ref1 + 41% FT	11.4	0.82	14.36	570	43.5	2	N/A
	SAJF1: 51% Ref3 + 49% HEFA	8.5	0.61	14.4	70	43.629	2	784.4
	SAJF2: 70% Ref4 + 30% HEFA	9.5	0.05	14.51	1	43.632	2.02	777.3
	SAJF3: 49% Ref3 + 34% Ref4 + 30% HEFA	15.2	0.64	14.04	70	43.358	N/A	761.1
ECLIF III [54]	Jet A-1	13.4	0.35	14.08	211	43.2	1.95	N/A

Experimental Campaign	Fuel	**Fuel properties**						
		Aromatics (% vol)	**Naphthalene (% vol)**	**Hydrogen (% mass)**	**Sulphur content (ppm)**	**LCV (MJ kg^{-1})**	**H/C ratio**	**Density (kg m^{-3})**
	100% HEFA-SPK	0.41	0.002	15.11	7	44.1	2.12	N/A

Table C.3 Summary of different experimental campaigns that identified a positive association between the fuel aromatic content and soot emissions emitted by aircraft gas turbine engines.

No.	Campaign	Ground /Cruise	Equipment	Fuel	Objective
1	NASA APEX [118]	Ground	Douglas DC-8, CFM56-2-C1	● JP-8, ● JP-8 with added sulphur, ● High aromatic Jet A-1	Evaluate the impact of fuel sulphur and aromatic content on soot and secondary particle formation.
2	Corporan et al. [223]	Ground	C-17 Globemaster III PW-100 (F117)	● JP-8a, ● JP-8b, ● 50% JP-8b + 50% HRJ, ● 50% JP-8a + 25% HRJ + 25% FT	Emissions evaluations on a military jet aircraft using different alternative fuels blends, including a hydroprocessed renewable jet (HRJ) fuel blend, and Fischer-Tropsch (FT) fuel.
3	Timko et al. [228]	Ground	PW308	● JP-8, ● 100% FT-SPK, ● 50% JP-8 + 50% FT-SPK	Measure effects of alternative fuels on the trace gas, non-volatile and volatile PM emissions performance from a business jet class gas turbine engine.
4	Timko et al. [224]	Ground	CFM56-7B	● Jet A & Jet A-1, ● Jet A-1 + FAME blends, ● 100% FT-SPK ● 50% Jet A-1 + 50% FT-SPK	Measure gaseous, volatile, and non-volatile pollutants using different alternative fuel types, in particular, the fatty acid methyl ester (FAME) jet fuel with negligible aromatics and increased oxygen content.
5	Corporan et al. [127]	Ground	● CFM56-7 ● CFM56-2 ● PW F117 ● PW TF33 ● PW308C	● JP-8 ● 50% JP-8 + 50% FT (Syntroleum) ● 50% JP-8 + 50% FT (Shell) ● 50% JP-8 + 25% HEFA (tallow) + 25% FT (Sasol)	Evaluation of five turbofan engines and one turboshaft engine to assess the impacts of alternative (non-petroleum) fuels on emissions and to support the certification of military aircraft using alternative fuel blends.
6	NASA AAFEX-I [149]	Ground	Douglas DC-8, CFM56-2-C1	● JP-8, ● FT-SPK (gas & coal) ● 50% JP-8 + 50% FT-SPK (gas) ● 50% JP-8 + 50% FT-SPK (coal)	Investigate the effects of alternative fuels on: (i) aircraft gas-phase and particle emissions; (ii) volatile aerosol formation in aging exhaust plumes; and (iii) the role of ambient conditions in influencing volatile aerosol emissions.
7	NASA AAFEX-II [53]	Ground	Douglas DC-8, CFM56-2-C1	● JP-8, ● 100% HEFA-SPK (tallow), ● 50% JP-8 + 50% HEFA-SPK ● FT-SPK ● FT-SPK with added sulphur	Investigate the effects of alternative fuels on: (i) aircraft gas-phase and particle emissions; and (ii) the role of sulphur in regulating sulphate emissions
8	NASA ACCESS-I [53]	Ground	Douglas DC-8, CFM56-2-C1	● JP-8, ● 100% HEFA-SPK (Camelina), ● 50% JP-8 + 50% HEFA-SPK	Ground-testing to support evaluation of alternative fuel effects on the aircraft exhaust composition and contrail formation.
9	A-PRIDE 7 [136]	Ground	CFM56-7B	● Jet A-1, ● Jet A-1 + Solvesso 150, ● Jet A-1 + Solvesso 150 naphthalene ● depleted	Examine the effects of increasing fuel aromatic and naphthalene content on aircraft nvPM emissions

No.	Campaign	Ground /Cruise	Equipment	Fuel	Objective
10	Lobo et al. [126]	Ground	Mixed turbofan aircraft engine (< 26.7 kN)	● Jet A-1, ● Sasol IPK	Measurement of nvPM emissions using a standardised sampling system to assess its suitability and limitations in evaluating different fuel properties.
11	NASA ACCESS-II [226]	Cruise	Douglas DC-8, CFM56-2-C1	● Jet A-1 (Medium- and low-sulphur), ● 50% Jet A-1 (low-sulphur) + 50% HEFA-SPK	Alternative fuel effects on the aircraft exhaust composition and contrail formation at cruise altitudes
12	ECLIF I [52]	Ground	Airbus A320-232, IAE V2527-A5	● Jet A-1 (Ref1 & Ref2), ● 59% Ref1 + 41% FT-SPK, ● 55% Ref2 + 45% FT-SPK, ● 86% Ref1 + 14% FT-SPK, ● FT-SPK	Quantify the impact of aircraft gaseous and particle emissions by systematically varying the fuel aromatic content.
13	CAAFCEB [227]	Cruise	Falcon 20, GE CF700-2D2 engine	● Jet A-1 ● JP-8, ● ATJ-SPK ● Jet A-1 + ATJ-SPK blend	Particle emissions and contrail measurements from a research aircraft burning an ethanol-based alcohol-to-jet (ATJ) SPK fuel blend and two conventional fuels.
14	ECLIF I & ECLIF II/ND-MAX [166]	Cruise	Airbus A320-232, IAE V2527-A5	● Jet A-1 (Ref1, Ref2, Ref3 & Ref4), ● 59% Ref1 + 41% FT-SPK ● 51% Ref3 + 49% HEFA-SPK ● 70% Ref4 + 30% HEFA-SPK	Evaluate the impact of biofuel blends on aircraft particle emissions and young contrail properties.
15	ECLIF II/ND-MAX [182]	Cruise	Airbus A320-232, IAE V2527-A5	● Jet A-1 (Ref3 & Ref4), ● 51% Ref3 + 49% HEFA-SPK, ● 70% Ref4 + 30% HEFA-SPK	Evaluate the impact of biofuel blends on aircraft particle emissions and young contrail properties.
16	EMPAIREX [140]	Ground	CFM56-7B	● Jet A-1 ● 68% Jet A-1 + 32% HEFA-SPK	Investigate the effects of an alternative fuel blend on nvPM mass and number emissions, and particle size distribution.
17	Zheng et al. [131]	Ground	Rolls Royce Tay combustor	16 aromatic species blended with a base C10-C13 straight-chain hydrocarbon solvent.	Evaluate the volume and types of different aromatic species in influencing the aircraft engine PM emissions.
18	ECLIF II/ND-MAX [119]	Ground	Airbus A320-232, IAE V2527-A5	● Jet A-1 (Ref3 & Ref4), ● 51% Ref3 + 49% HEFA-SPK, ● 70% Ref4 + 30% HEFA-SPK, ● 49% Ref3 + 34% Ref4 + 17% HEFA-SPK	Examine the effects of fuel composition on aerosol and trace-gas emissions on the ground.
19	ECLIF III [54]	Cruise	Airbus A350-941, Rolls-Royce Trent XWB-84	● Jet A-1, ● 100% HEFA-SPK	Examine the effect of burning 100% SAF on young contrail properties and microphysics

State-of-the-art lean burn combustors

Many modern gas turbine systems in civil turbofan engines feature lean burn technology based around staged fuel atomisers allowing combustion to be carried out at leaner conditions across the entire flight cycle and at all power conditions. This is achieved by adding a greater portion of air, greater than 70% of the combustion air mass flow directly into the fuel injector and mixing with fuel, either before the inlet to the combustor (called premixing) or downstream of the fuel injector tip as separate streams.

Lean burn combustion technologies all exhibit a rich burning pilot zone, which remains ignited with a robust, well controlled flame throughout ground idle and all flight phases. The difference between rich burn systems and a lean burn system is the presence of a lean injection system in the combustors main combustion zone which is only fuelled during higher power modes as shown by Mongia [229].

There have been several iterations of lean burn combustion systems in service from the two main North American civil turbofan aeroengine manufacturers, General Electric (GE) and Pratt and Whitney. Mongia details the development of GEs lean burn technology from early RQL single annular combustors followed the concept of splitting the combustor into two, radially adjacent separate zones in the Dual Annular Combustor (DAC) and finally the Twin Annular Premixing Swirler (TAPS) technology now fitted to many modern GE and CFM engines [229].

NASA and GE have developed the Twin Annular Premixed Swirler (TAPS) injector which has been installed on CFMS LEAP engines and others. This novel technology allows a rich pilot flame to remain lit when the lean, premixing (secondary) combustion zone runs only at higher power conditions. The technology is arguably the most advanced lean burn atomiser currently in service across the global civil aviation fleet with the most flying hours of any lean burn atomiser.

The design concept behind this atomiser is to combine two separate fuel circuits, each with a distinctly different atomiser installed into one atomiser/atomiser body. The pilot atomiser is similar to a conventional style rich burn atomiser which runs rich during low power conditions. The secondary lean premixed atomiser is a radially directed cross flow liquid jet, directed perpendicular to the incoming swirling air from the combustor dome’s cyclonic mixers. A schematic for this injector can be seen in Figure C.2 from the work of Stickles et al. [230].

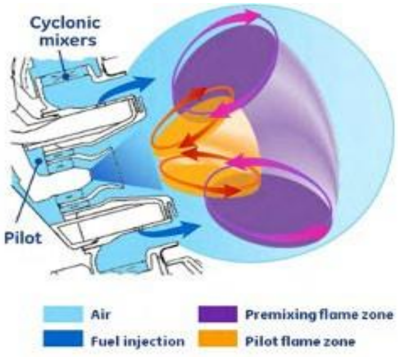


Figure C.2: TAPS injector diagram. Light blue = air, dark blue = fuel injection, purple = main/premixing flame air zone, orange = rich, pilot flame zone. White sections outlined in black represent fuel injector hardware. From the work of Stickles et al. [230]

Figure C.2, shown in Lefebvre and McDonell [105]) and Figure C.3 from the work of Fyffe (Rolls- Royce Plc) [108] illustrate lean direct injection atomisers with twin fuel circuits (pilot and main) like GEs TAPS Lean premixed pre-vaporised (LPP) injector shown in the work of [105]. This system achieves lean burn combustion by distributing the fuel more evenly throughout the cross section of the combusting air. As a result, localised fuel rich pockets of mixture are avoided, in turn reducing hot spots which occur as the mixture passes through the stoichiometric equivalence ratio while burning. The result is that NO_x emissions are reduced by spraying the fuel more evenly into the combustor and metering or staging some fuel circuits at higher power conditions to reduce emissions by keeping the combustor heat release as evenly distributed as possible. The combustor volume downstream of the injector must provide sufficient residence time to avoid UHC emissions by allowing sufficient residence time to burn fuel before entering the nozzle guide vanes downstream of the combustor at all flight conditions. As such, combustion system design is a careful trade-off between the available space claim (combustor volume) between the compressor and the turbine, fuel systems and the given cross section available for the combustor in addition to the injector design.

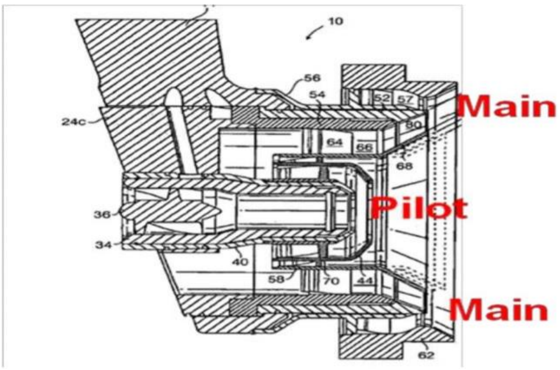
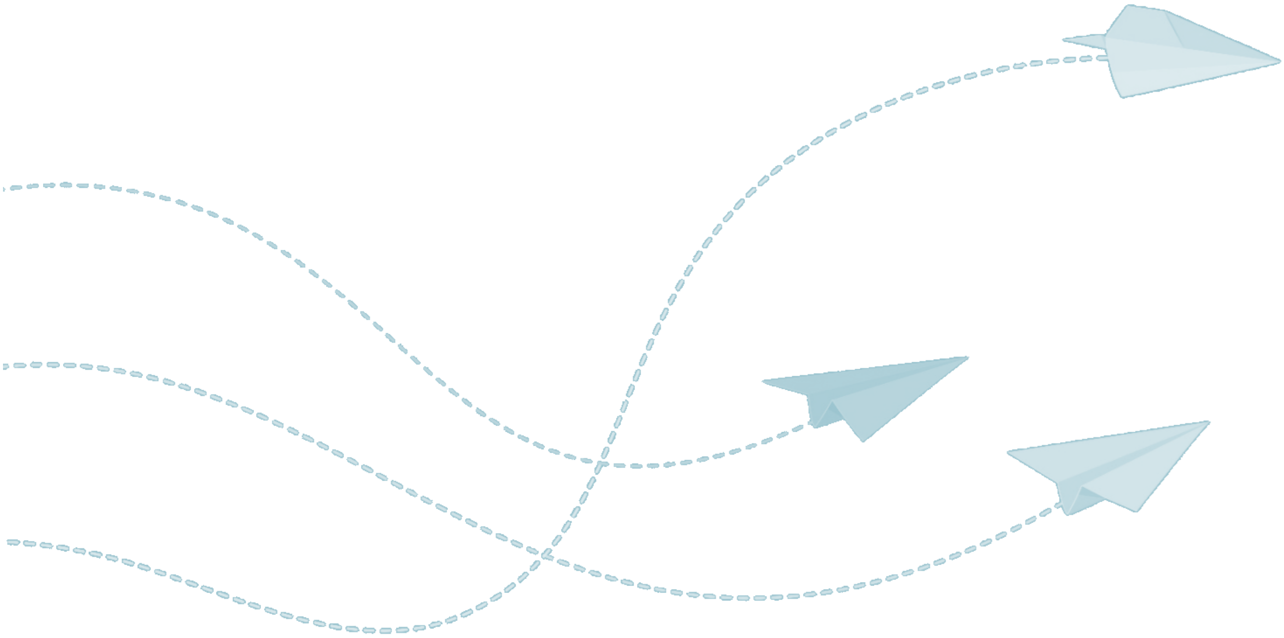


Figure C.3: Rolls-Royce Lean Direct Injection (LDI), Staged axial fuel injector with concentric pilot and main prefilming air blast atomisers. Image from the work of Fyffe et al [108]



Appendix D: *Closing the gap* jet fuel test campaign

Introduction

A comprehensive literature review has highlighted gaps in our understanding of fuel chemical composition's impact on soot and ice crystal formation. Closing these knowledge gaps is crucial for addressing non-CO_2 emissions and understanding how jet fuel composition, particularly how types of aromatics influence soot particle formation is essential. To carry out this *Closing the Gap* test campaign, a brief test was planned to provide additional information on impact of aromatics content of Jet A-1 fuel on non-CO_2 emissions. Five types of jet fuels were selected considering an envelope of variations in their aromatic component. The fuels were designed and blended to investigate the effects of aromatics on soot particle emissions. The sulphur content of the jet fuels was kept low to explore the influence of the changing hydrogen content while controlling for the sulphur effects on soot particle activation. The result from these tests paves the way to provide additional information on the knowledge gap relating to soot-forming tendencies of jet fuels and the recommendation of guidelines for fuel specification with the objective to significantly reduce the climate impacts of aviation fuels. During the test campaign, in addition to measuring particle emissions (mass and number) of a large variety of jet fuels with a wide range of aromatics percentage (hence different H/C ratio), the other properties such as density and viscosity, which are important from an engine and aircraft compatibility and operability standpoint were also investigated.

The University of Sheffield's Energy Innovation Centre conducted comprehensive tests on gaseous and particulate emissions from jet fuel with varying aromatic content. Five Jet A-1 fuel samples + HEFA with 0% aromatics were used, with aromatic content ranging from 0% (HEFA) to 15.6%. Additionally, fuel chemical analysis included assessing different aromatics content and the H/C ratio. In contrast, the baseline fuel was standard JetA-1 with 14.5% aromatics, sourced from a commercial airport. This baseline fuel was delivered in batches, each consisting of four 200-litre drums. The characterisation of the baseline fuel was meticulously assessed at the SAF- IC characterisation lab.

The primary objective of the testing was to thoroughly examine the impact of aromatic concentration and H/C ratio on particulate emission characteristics and non-CO_2 gaseous emissions. This involved using the LII 300 particulate analyser provided by Rolls-Royce, in conjunction with the University of Sheffield's Dekati ELPI impactor. These tools facilitated the assessment of size and number distribution of particulate emissions.

Additionally, PM emissions were rigorously evaluated using additional equipment, including the Scanning Mobility Particle Sizer (SMPS) and Transmission Electron Microscopy (TEM) analysis. The conventional gas analyser facilities were used to measure NO, NO_2, CO and SOx.

This report exclusively focuses on the results obtained by the University of Sheffield, providing a detailed examination of the impact of aromatic content and H/C ratio of jet fuels on gaseous and particulate emissions.

Experimental setup and deliverable

Auxiliary power unit (APU): Progressing towards recommendations for the impact of aromatics in jet fuels to tailor them towards minimal non-CO_2 effects is crucial and could have a major impact on aviation decarbonisation strategy. This would help to close the gap between the different previous test campaigns involving different fuels, and to better understand the impact of those parameters on soot emissions, contrail properties and their effects on climate.

The experimental setup was designed to ensure the accuracy and reliability of the emissions data collected during the testing process. A Honeywell 131-9A APU was deployed to test the fuels at two different loading conditions. Using advanced measurement and analytical methods available in SAF-IC fuel characterisation laboratory.

The B-variant of the 131-9 APU is used in Boeing 737-600/-700/-800 aircraft, while the A-variant is used in Airbus A319/20/21 models. The APU serves as a versatile self-contained power unit offering both shaft and pneumatic power, which are regulated through a system of electronic, hydraulic, and electro-mechanical controls. The APU can provide power while the aircraft is on the ground or during flight and consists of two main sections: the load section, housing the gearbox and load compressor, and the power section. Each of these components has a specific role in the APU's operation and performance.

State-of-the-art facilities was used to measure gaseous emissions such as $CO/SO_2/CO_2/CH_4/O_2/NO/NO_2$. The Dekati ELPI+ was used to assess the size and number distribution offering real-time measurement capabilities across 14 distinct size fractions, ranging from 6 nm to 10 µm.

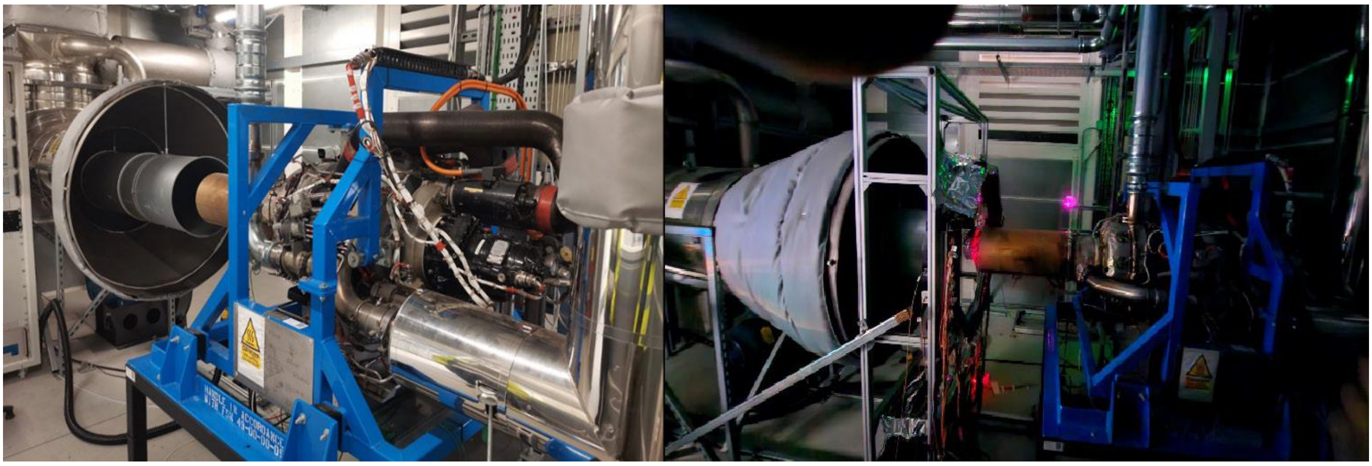


Figure D.1: The Honeywell 131_9A APU at the Energy Innovation Centre, University of Sheffield

Analytical studies of jet fuels with variable aromatics content

(a) **Comparative analysis of jet A-1 fuels with different aromatic content using multi- dimensional chromatography:** Hydrocarbon chemistry is an important fuel property describing the chemical makeup, distribution, and ratio of various hydrocarbons present in conventional jet fuel. Typically, petroleum derived aviation fuel is composed of a mixture of normal paraffins (n-paraffins), isoparaffins, cycloparaffins, and aromatics. Hydrocarbon composition was determined using the SAF-IC GC×GC-ToF-MS instrument method that provides hydrocarbon composition as a function of carbon number.

The purpose of this section is to showcase the comprehensive qualitative chromatographic analysis of Jet A-1 fuels with different aromatic contents. This type of analysis is necessary, since most of the time, traditional GC analysis is not sufficient to resolve complex samples, such as jet fuel, containing hundreds/thousands of peaks that will results in several chromatographic coelutions.

GC×GC analysis works by trapping the eluting analytes from the first-dimension column in the modulator and successive re-injection onto the second-dimension column of different polarity results in a tremendous higher peak capacity. However, it is essential to realise that even with the power of a GC×GC chromatographic separation, co-eluting peaks are still prevalent in such complex samples. Therefore, the automated deconvolution of the resulting mass spectra provides an additional benefit to this system solution. Resulting data is displayed in three-dimensional chromatogram images (contour plots or 2D plot) to aid understanding and explanation.

(b) Analysis of trace element content via ICP-OES: The SAF-IC laboratory is equipped with a Spectro ARCOS inductively coupled plasma – optical emissions spectrometer (ICP-OES), to enable simultaneous measurements of up to 64 elements in liquid samples across a range of applications. It uses inductively coupled plasma excitation and a semiconductor-based detector system for quantitative and semi-quantitative analysis. ICP-OES was used to check the impact of post treatment of jet fuel (as a part of reducing aromatic content) at refineries on metal contamination.

Experimental results and discussion

Deliverables of the jet fuel test campaign *Closing the Gap*:

- Determine the primary chemical component of jet fuel's propensity to generate soot by further elucidating the effects of naphthalene and/or the H/C ratio for a wide range of fossil Jet A-1.
- Sort the fuels in the fuel matrix based on their propensity to form soot and evaluate how this propensity changes in response to changes in the aromatic components.
- Gain a clearer knowledge of the nvPM sensitivity to the chemical components of jet fuels assessed in earlier research, which is reviewed in this report, as well as new data obtained from this test programme for fuel compositions not previously examined.
- All experiments included measurements of particles (nvPM) and trace gases (NO, NO_2, CO, and UHC), and as anticipated the fuel types had little effect on gaseous emissions.
- Achieve an assessment of impact of aromatics concentration (energy density) on fuel efficiency.
- Gather information on a more precise technique to forecast a jet fuel's propensity to generate soot based on its chemical composition, with an emphasis on aromatics and naphthalene in particular.

GC-GC-ToF-MS: Leco ChromaTOF software was utilised for instrument control and data processing. The National Institutes of Standards and Technology (NIST) mass spectral library was used for peak identification. Efficiency as peak capacity in gas chromatography is expressed in terms of by how many resolved peaks can fit into a certain time period. Further detailed description of the analytical procedure and theoretical calculation is available by request (contact saf-ic@sheffield.ac.uk). The results of qualitative analysis of three types of Jet fuel are presented below:

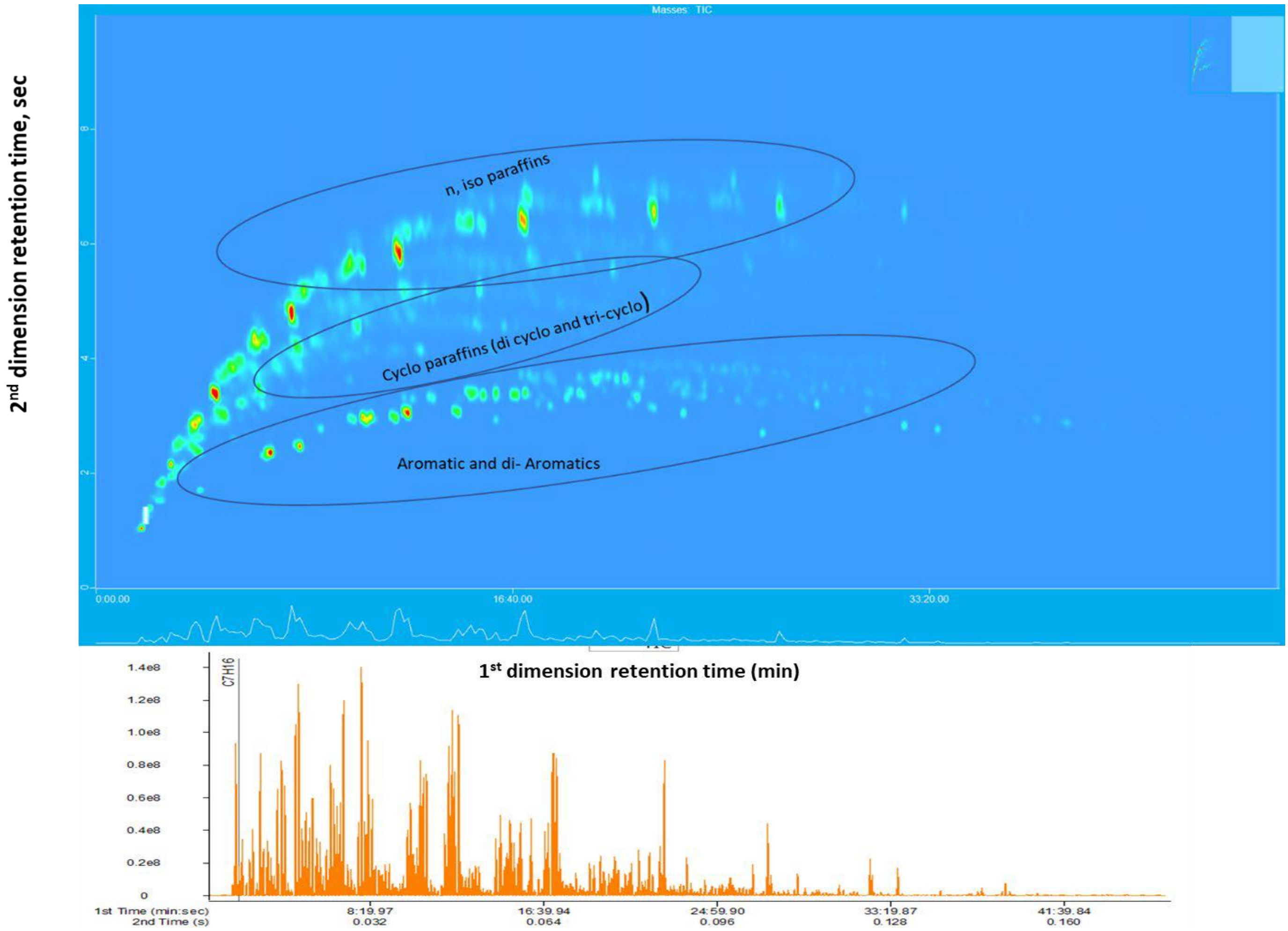


Figure D.2: Illustrating the different classes of hydrocarbons constituents in Jet A-1. The separation along the x-axis (1st dimension retention time) is in the increasing order of carbon atoms, whereas separation along the y-axis (2nd dimension retention time) is on the basis of polarity.

Figure D.2 shows a typical GCxGC-ToF-MS plot from Jet A-1 contour plot from the analysis. A summary of the composition breakdown by weight percent is shown in Table D.4, which shows the fuel is comprised of iso-paraffins, n-paraffins, cycloparaffins and aromatics, the primary constituents in petroleum derived Jet A-1 fuel. As can be seen from the data, the jet A-1 fuel is predominately cyclo-paraffinic in nature, with lower levels of normal and I-paraffins. The aromatic content of the Jet A-1 fuel was determined to be 14.53% by weight and shown to be primarily composed of alkylbenzenes (mesitylene). Aromatics are important to elastomeric seals in an engine. Seals swell in the presence of aromatics; therefore, controlled seal swell is important.

Jet A-1	**n-paraffins**	**I-paraffins**	**Cyclo-Paraffins**	**Mono-aromatics**	**di- aromatics**	**Poly-aromatics**
% by Mass	23	28	32	13	1	0

Low aromatic jet fuel: Figure D.3 illustrates a three-dimensional plot of resolved peaks in terms of 1st dimension retention time, 2nd dimension retention time and intensity of the detection ions by the MS detectors, where the intensity is a measure of amount of hydrocarbon species in the mixture. Unlike conventional Jet A-1, low aromatic jet fuel sample (7.1% aromatics) is rich in n- and iso alkanes with insignificant amount of cyclo-paraffins. Furthermore, in contrast to the Jet A-1 where the distribution of carbon atoms peaks at C12, the low aromatic fuel shows significant concentration of heavier hydrocarbons towards the end of plot. In addition, it was noted that the fuel sample contains minimal carbon number (over C16) that will have impact on low temperature properties.

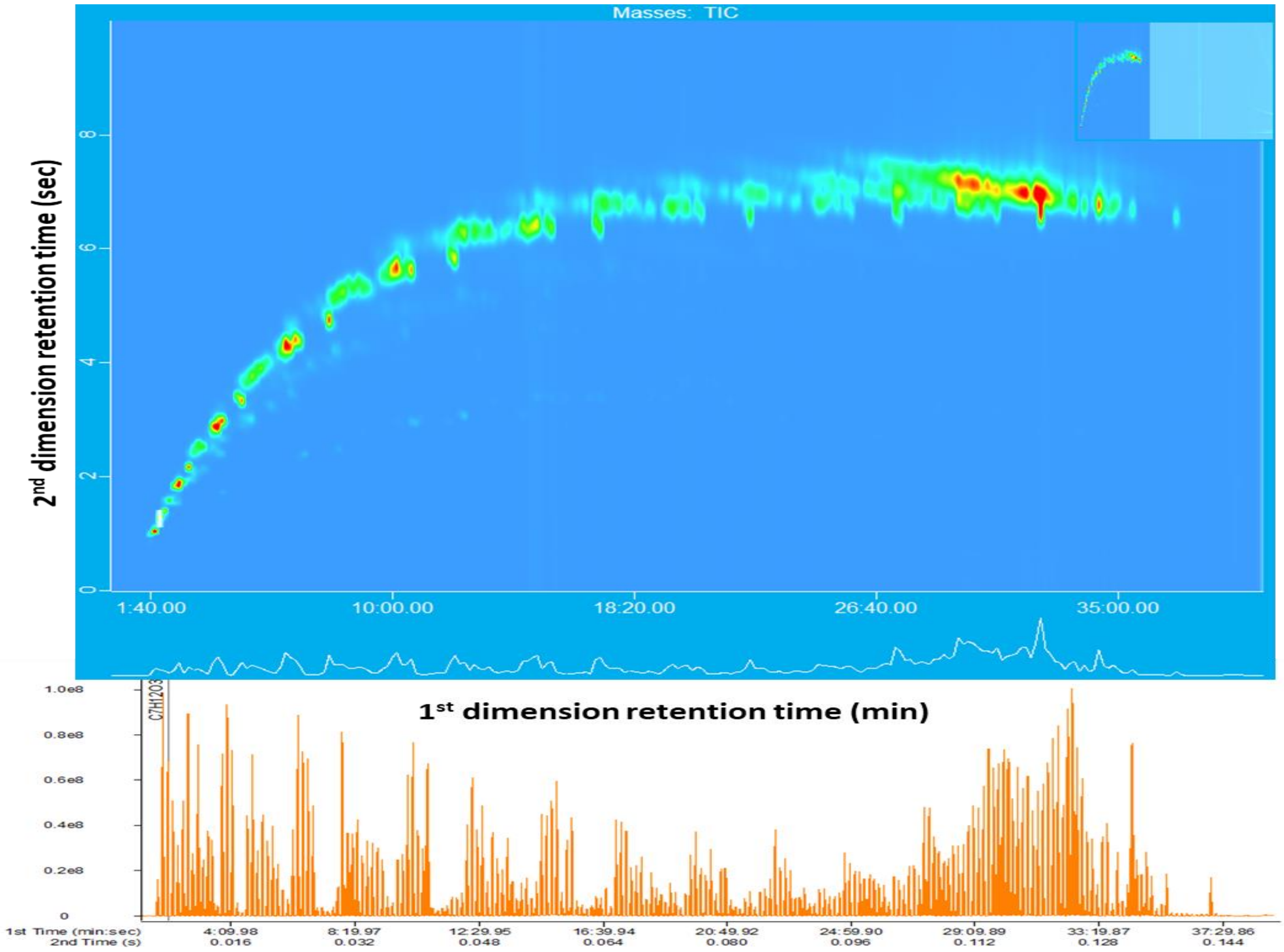


Figure D.3: Contour plot of different classes of hydrocarbons in low aromatic fuel

Analysis of trace element content via ICP-OES: ICP-OES can be used for two key applications, namely determinations of trace metals in (i) acid/water samples and (ii) organic/fuel samples. The system is supplied with sample introduction systems specific to each application, including a dedicated spray chamber and nebuliser designed specifically for fuels. The element calibrations, test methods and operating conditions have been further optimised based on fuel properties, including for both viscosity and vapour pressure typical of aviation fuels. With multiple spectral lines available for each element, those with minimal interferences can be selected to enhance measurement accuracy and precision.

Figure D.4 highlights typical results of analysis conducted on a Jet A-1 fuel samples with varying aromatic content + HEFA (0% aromatics) in the SAF-IC laboratory, including the concentration and of up to 50 metals detected in aviation fuels. The analysis of all fuel samples revealed that they contain trace metals at levels below the maximum allowable concentration. Additionally, the fuels with low aromatic content (ultra-low sulphur content for HEFA 0% aromatic) and lower levels of inorganic and organic compounds compared to conventional Jet A-1 fuel. These differences can be attributed to the hydro processing severity however we must mention that there is uncertainty at very low concentrations.

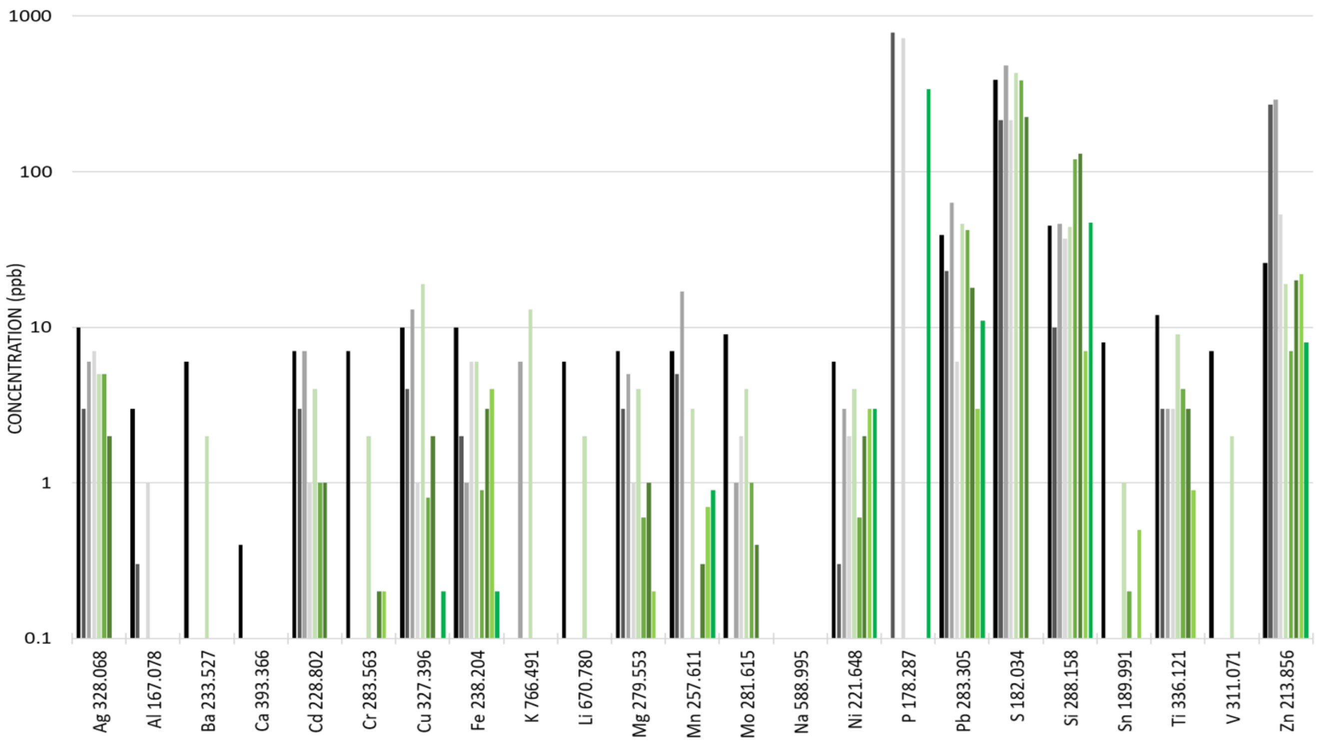


Figure D.4: Black columns: Jet A-1 (15.3% Aromatics), Light Grey columns: Jet A-1 (14.7% Aromatics), Grey/Green columns: Jet A-1 (14.5% Aromatics), Light Green columns: Jet A-1 (13.05% Aromatics), Dark Green columns: Jet A-1 (11.6% Aromatics), Luminous Green columns: et A-1 (7.1% Aromatics), Bright green columns: 100% HEFA (0% Aromatics)

Conventional jet fuels often contain a class of organic compounds consist of a sulphur-hydrogen group (SH) bonded to a hydrocarbon chain, forming R-SH. The presence of these chemical species in fuel can increase the reactivity of the compound, potentially leading to corrosive attacks on fuel-wetted metallic components within the fuel system. Sulphur was found in high concentrations in conventional Jet A-1 fuel samples – (PPM levels as opposed to PPB levels for the other elements) but reduced to 66% for Jet A-1 with 7.1% aromatic content (The HEFA samples were below the detection limit for S). Results obtained from ICP-OES test indicate that:

- Fe was present but at relatively low levels (at 10 ppb or less) across all samples (some of the RSD% were quite high, especially for those that were close to the detection limit or lower calibration range).
- Mg was also found in low concentrations (up to 7 ppb) in the Jet A-1 but reduced as aromatic concentration decreased and very low (often below the detection limit) for the HEFA.
- Zn was present in all samples, although much higher for most of the Jet A-1 samples and very low for the low jet fuels with 7.1% aromatics.
- Cu was quite low for the low aromatic content jet fuel, and only found in max concentrations of 13 ppb in the conventional Jet A-1
- Mn was very low for all samples, except 17 ppb in one of the conventional Jet A-1 samples
- Ag, Cd, Ni, Pb, Si and Ti were found in similar levels for each of the fuels - usually slightly higher for conventional Jet A-1

APU test results of impact of aromatics on Non-CO_2 emissions:

During the *Closing the Gap* jet fuel test campaign, we tested all four jet fuel samples with varying aromatic content alongside conventional Jet A-1 fuel. The goal was to assess the impact of aromatic concentration on engine systems under realistic conditions. The APU rig test program conducted activities to enhance our understanding of the relationship between fuel composition and combustor performance, operability, and gaseous and particulate emissions by measuring PM emissions, NOx from exhaust plumes of the APU engine using a set of state-of-the-art instruments. The sampling methodology can be provided by contacting the consortium members. In addition, the impact of varying aromatic content in jet fuels on fuel flow was investigated.

To better comprehend the influence of aromatic concentration on conventional jet fuel properties, we conducted an assessment of emissions and fuel efficiency performance. Tests were carried out at critical APU operating points: “Ready to Load (RTL)” and “Full Load (FL).” Figures
D.5 onwards display the experimental results for particulate emissions, NOx and fuel efficiency. These results are then compared to the baseline Jet A-1 fuel and other previously tested alternative fuels (such as HEFA).”

Figure D.5 (a) indicates the particulate mass concentration (reported in mg/m^3 by the LII 300) for five tested fuel samples with varying aromatic contents (0%, 7.10%, 11.6%, 13.05%, and 14.5%). The x-axis represents the percentage of aromatic content, while the y-axis represents the mass concentration. The graph suggests a **positive correlation** between aromatic content and particulate mass concentration at RTL condition. Similarly, Figure D.5(b) presents the results for the full-load (FL) condition.

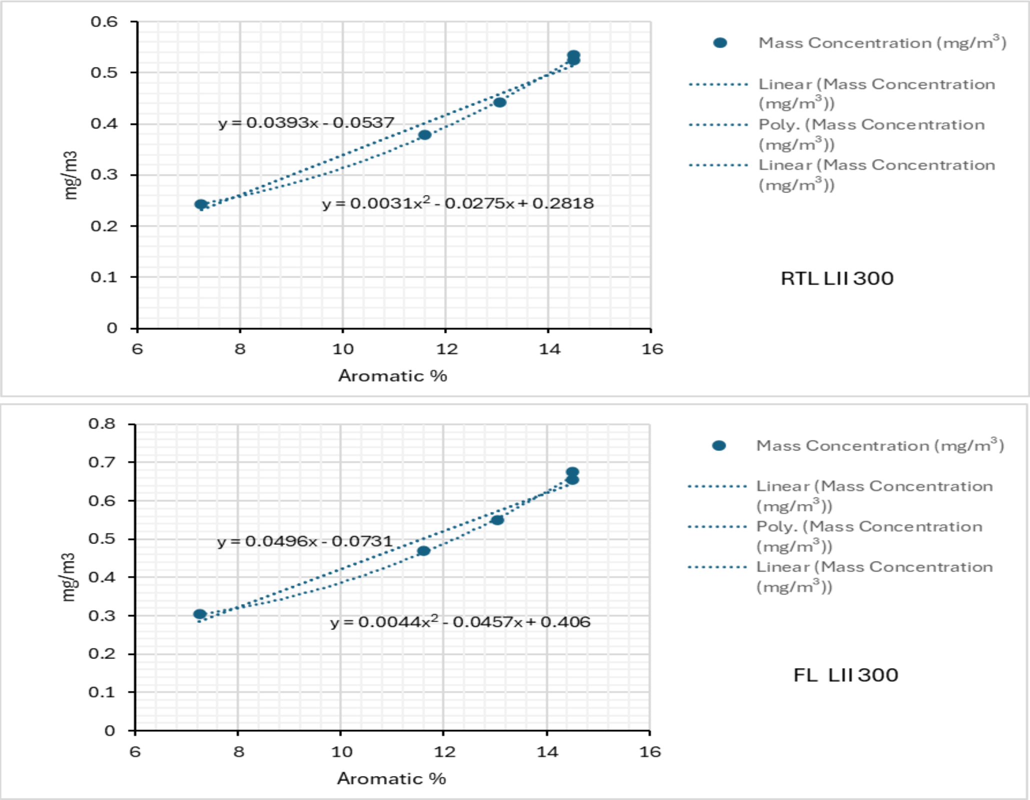


Figure D.5 (a-b): particulate mass concentration for five tested fuel samples with varying aromatic contents (0%, 7.10%, 11.6%, 13.05%, and 14.5%)

The APU exhaust gas was extracted via the gas sampling probe under two test conditions (RLT and FL) and analysed using a NOx analyser. Figure D.6 illustrates the measured NOx emissions for both operating conditions.

Interestingly, the NOx emissions were quite similar across all samples with varying aromatic content, and no significant differences were observed. The NOx emission Index (E_{NOx}) did not change significantly for the fuel samples tested. However, when considering the reduction in fuel consumption, the NOx Emission Factor (EF_{NOx}) was lower for Jet A-1 fuel with lower aromatic content.

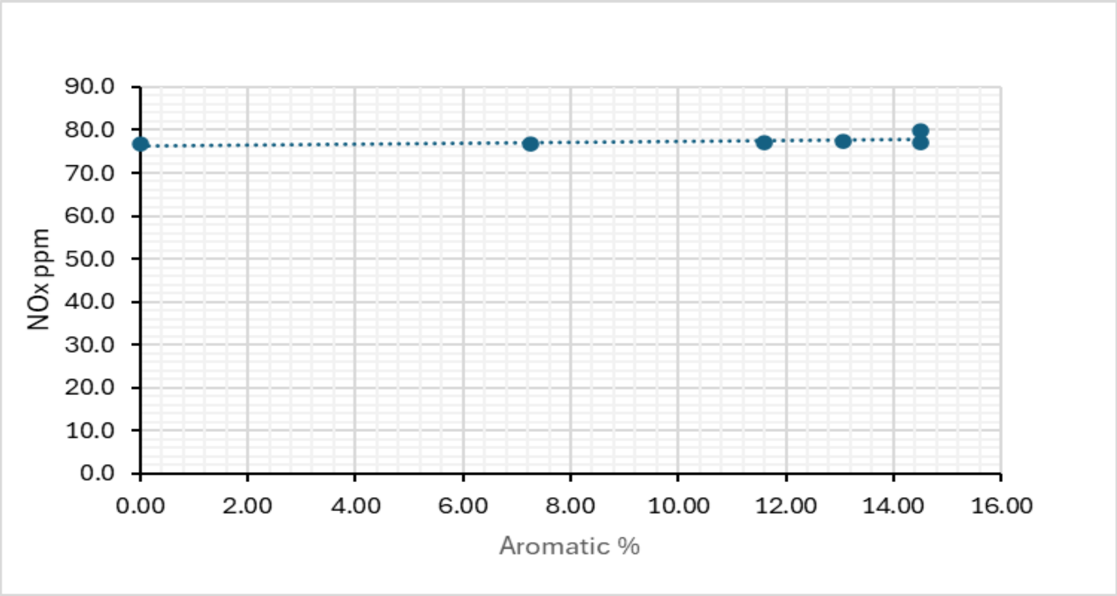


Figure D.6: Impact of conventional jet fuel aromatic content on NOx emission

Impact of fuel aromatics on fuel consumption: The engine showed no change in behaviour from an operational perspective. The result from these runs indicates reduction of lower fuel flow for fuels with lower aromatics. To reach designated or nominal temperature levels, the fuel mass flow rate directly depends on the fuel's energy content, or the heat of combustion. In this sense, the reduced fuel consumption and higher energy content by mass of fuel with lower aromatics have a beneficial impact on the pollutant emissions such as CO_2, H_2O, and SOx. However, the chemistry of pollutant generation is extremely non-linear and sensitive to even minute variations in the fuel's chemical makeup. Therefore, it could be concluded that using lower aromatic jet fuels may impact the overall flight efficiency (CO_2 and non-CO_2 species produced per passenger per kilometre, all under similar condition) will depend on take-off weight and thrust needs for a flying which affect the trip's overall energy consumption and emissions. A fraction of emissions is correlated with the mass flow rate of fuel. Particulate formation is one of the key components that relates the fuel composition. Further investigation is planned for in depth analysis of impact of types of aromatics on fuel consumption and energy density. Figure D.7 (a-b) indicates that fuel consumption reduced for fuels with lower aromatic content (hence higher H/C ratio and energy density).

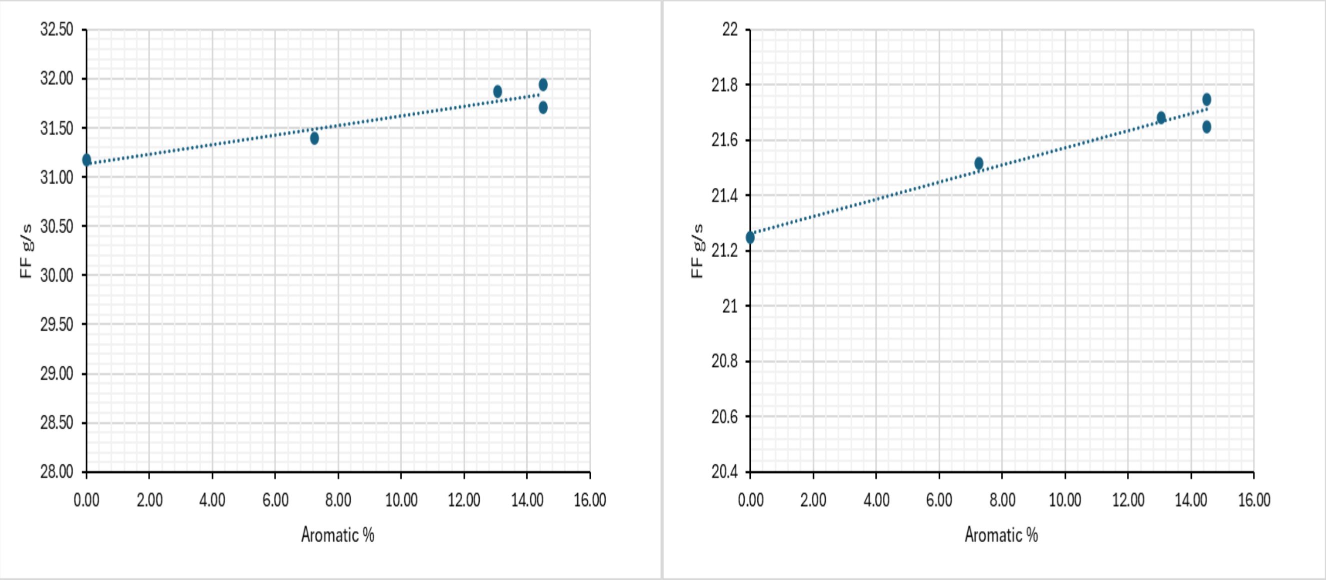


Figure D.7 (a-b): Impact of aromatic content of conventional jet fuel on fuel consumption. a = FL, b = RTL.

Concluding remarks

The *Closing the Gap* jet fuel test campaign aimed to investigate the impact of aromatics content on non-CO_2 emissions and fuel performance. The findings from this very brief test campaign provide additional technical insights, supporting the long-term goal of investigating reducing aromatics in jet fuel to mitigate non-CO_2 emissions from the aviation sector. Key findings include:

1. **Reduction in nvPM emissions:**
    - Jet A-1 fuel with 13.1% aromatics showed 19% reduction (in mass) and Jet A-1 fuel with 7.1% aromatics achieved a 58% reduction (in mass) compared to conventional Jet A-1 with 14.5% aromatics (at full load condition).
2. **Fuel consumption reduction:**
    - Jet A-1 fuel with 13.1% aromatics demonstrated a 0.5% decrease in fuel consumption and Jet A-1 fuel with 7.1% aromatics demonstrated a more significant 1.8% reduction in fuel consumption compared to conventional Jet A-1.
3. **NOx emissions and aromatic content:**
    - There was no significant change in NOx emissions based on the aromatic content of the fuel.
4. **NOx emission factor improvement:**
    - The NOx emission factor (EF_{NOx}) decreased by 2.5% when Jet A-1 fuels reduced their aromatic content from 14.5% to 7.1% (due to the increase in calorific value and reduction in fuel mass flow rate).

These findings underscore the importance of monitoring and potentially controlling the aromatic content of jet fuel to enhance environmental performance. By reducing aromatics, the aviation industry can contribute to lowering its overall climate impact beyond CO_2 emission

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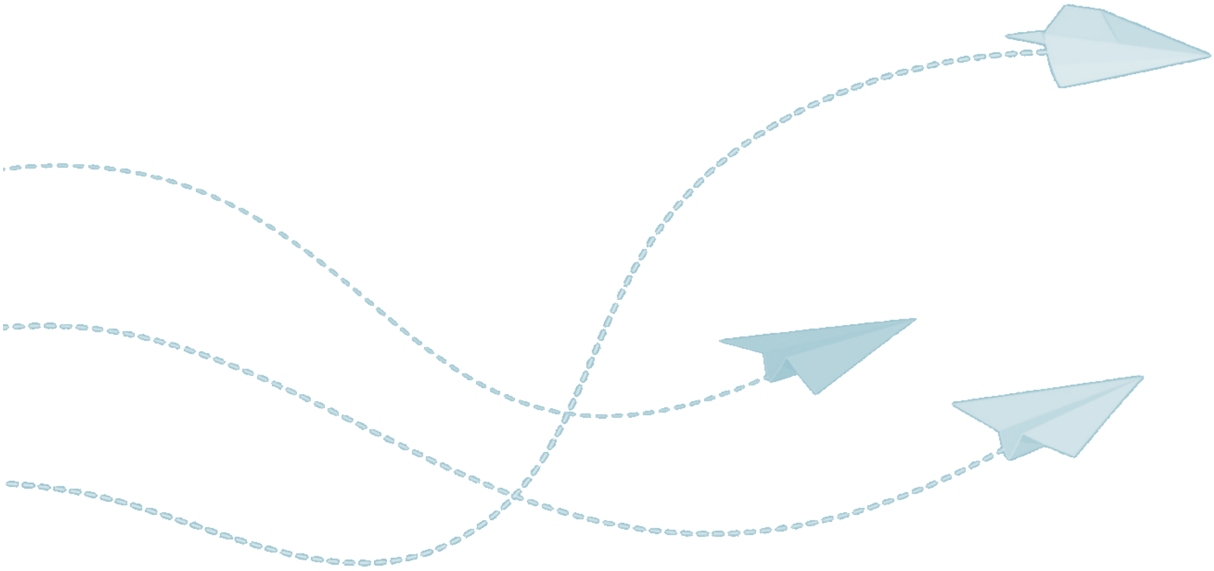

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