16TH INTERNATIONAL CONFERENCE ON STABILITY, HANDLING AND USE OF LIQUID FUELS
Long Beach, California, USA
September 8-12, 2019

Abstract Summaries

Chevron Award of Excellence in Honor of John Bacha:

PROFILING OF THE ORGANIC NITROGEN COMPOUNDS IN MARGINALLY STABLE DIESEL FUELS USING GCXGC-NITROGEN CHEMILUMINESCENCE DETECTION (NCD)

Rachel D. Deese, Robert E. Morris, Thomas Loegel

Previously, a set of low sulfur diesel fuels from the Western Pacific region were found to be unstable during storage although they passed all standard specification tests, thus defining them as “marginally stable”. This sample set was found to have high nitrogen content and studies on these fuels by liquid-liquid phase extractions, GC-MS, and GC-nitrogen phosphorous detection (NPD) revealed a correlation between the basic nitrogen compounds (BNCs) in these fuels and the formation of high levels of particulates in storage. In this study, a two-dimensional gas chromatography with nitrogen chemiluminescence detection (GCxGC-NCD) methodology was developed and validated to more extensively characterize the different classes of organonitrogen compounds in the marginally stable diesel fuels. The findings indicated that the basic nitrogen compounds are not unique to the marginally stable fuels; however, it did identify a lighter polar organonitrogen fraction that had previously not been observed. A survey of stable diesel fuels indicated that this light organonitrogen fraction was unique to the marginally stable fuels. If this is found to be universally applicable, this light polar nitrogen fraction may serve as an indicator of potentially unstable diesel fuels. Compared to the previous nitrogen detection methods, the GCxGC-NCD method has greater compound separation abilities and neat fuels can be injected onto the columns so no sample preparation is involved. Overall, the GCxGC-NCD method has shown to be a valuable tool to enhance our understanding of the chemistry of organonitrogen species and their impact on fuel stability.

SESSION 1: FUEL SUPPLY CHAIN STORAGE, HANDLING AND LOGISTICS

THE EDF ENERGY APPROACH TO FUEL OIL MANAGEMENT WITH PARTICULAR FOCUS ON THE PROCESS OF REVIEWING INDUSTRY-WIDE EXPERIENCE

Carl M Atkinson

On a nuclear power station most plant systems fueled by gas oil are deemed essential from a nuclear safety perspective and whilst redundancy is inbuilt in all of these systems, it is limited

conservatively. Essentially, these plant systems must have a high level of reliability and availability. Since the gas oil is a common feature across these systems, any inherent shortfall in its quality will have a potential to adversely affect the availability for some, if not all, of the associated fuelled plant items which, in the worst case could deem an entire system unavailable. The nuclear safety consideration, therefore, focuses on the availability of a viable fuel whilst ever there is a potential for it to be required. It is therefore important to ensure that the procurement, supply, management and storage of gas oil is governed by robust mandatory specifications and that these are periodically reviewed to ensure that they remain current and relevant. The problem for EDF Energy is that gas oil can be, and is, stored for considerable periods of time, into many years. Across its nuclear fleet there are a considerable number of storage tanks comprising many different designs and located in a very broad range of environments. Equally, the turnover of fuel within these tanks varies considerably dependent on the plant system. Consequently it is essential that EDF Energy is aware of current environmental thinking and changing technology and the ability to assess any potential threat to safety related functions. An overview of the EDF Energy approach to fuel oil management is described with particular focus on the process of reviewing industry-wide experience.

DIESEL FUEL FLASH POINT REDUCTION CAUSED BY TRANSPORT SWITCH LOADING AND SPLIT LOADING- A WARNING!!!

Howard Chesneau

Gasoline apparently is the main source of contamination in diesel fuel at the retailers. The contamination is most likely due to the switch loading – hauling gasoline prior to hauling diesel fuel or split loading where a single tanker has compartments carrying different types of fuel. As we know, diesel flashpoint is one of the important parameters for determination of its use. In FY2015, Georgia Department Agriculture (GDOA) issued 229 stop sales of diesel fuel to the retailers, which was more than the stop sales due to sediments or water. A designed experiment (DOE) was conducted in the Georgia Department of Agriculture State Fuel Laboratory at Tifton to determine factors that may significantly depress the flashpoint of diesel. The experiment was conducted by Karsen Wynn, an intern at the Fuel Laboratory. A simple three factorial design experiment was selected to investigate the effect of flashpoint on 1) diesels with different flashpoints, 2) diesels with different amount of gasoline contamination (from 0.25 % to 0.75 vt%), and 3) diesel contaminated with summer vs. winter grade gasoline. Additional field studies were conducted to verify actual events. This poster will show what was found and alert both suppliers and consumers of the potential issues. It will also establish possible links as to how ethanol may be entering the diesel fuel systems contributing to the increase of corrosion episodes attributed to ULSD.

SESSION 2: FUEL CONTAMINANTS

ADVANCES IN AVIATION FUEL WATER SEPARATION TESTING

Alan J. Fougere, Ian Mylrea

The initial work that lead to the first published laboratory based water separation test method commenced in 1961 and culminated in ASTM D2550 (WSIM) in 1966. That pioneering work lead to the development of the scale, based on a strong surfactant, upon which all other water separation tests were based. ASTM D3948 and D7224 followed, also based on the same scale, which used a smaller sample and took less time. Over several years jet fuel specifications introduced the tests to protect the market from fuels which would not separate water easily. Recent issues resulting in the planned removal of Filter Monitors has heightened the importance of water separation method performance. ASTM D8073 / IP624 is a more recent development, also using the same strong surfactant scale. This paper discusses all test methods, industry experiences, and, includes the latest industry test data and developments.

THE MANAGEMENT AND DETECTION OF TRACE FREE WATER IN AVIATION FUEL

Steve Anderson, Alisdair Clark, Michaela Seebold, Michael Zahnhausen

Water represents the most abundant liquid on the Earth, covering 71% of the planet's surface and a vital building block for life. The molecular structure of water also offers hydrogen bonding, an attribute which allows the chemical to exist as solid, liquid or gas depending on ambient conditions. However, from an Aviation perspective, these attributes make water a challenging contaminant to manage in fuel supply. Product may enter refinery production tanks dry, fresh from distillation units, but instantly adsorb moisture from the air in tank ullage or condensed water in tank heels. This challenge continues along the distribution chain to point of use. While soluble water in aviation fuel is unavoidable, excess free water represents a risk for flight operations through excess weight, no energy content and freezing to solid at altitude with the potential to block filters / fuel lines. To manage this hazard the Aviation Industry have developed technology to reduce free water in fuel, for example EI 1581 Water Filter – Coalescers and set stringent limits, for example via IATA and ATA103. Field test methods have also been developed to detect any trace water remaining. In this paper, various such test methods are assessed in a laboratory environment using a defined system to evaluate performance. Work highlights the challenge of such studies, featuring meta-stable systems at low contaminant concentration, and the different detection approaches available.

POTENTIAL IMPACT OF GREASE ON JET FUEL QUALITY

Daniel E. Kadlecek

The jet fuel distribution system includes equipment such as valves and swivel joints that requires lubrication. Sometimes this is accomplished with the fluid (jet fuel) that is being moved, but often the equipment requires a lubricant. Greases are typically used due to their viscosity and

durability in medium to high load applications. Unfortunately, there is usually only a single barrier (i.e. gasket or o-ring) between the grease and the jet fuel in this equipment. If this barrier were to fail, there could be contact between the grease and jet fuel. It is important to understand what potential impact grease could have on jet fuel quality in this scenario. This presentation will highlight research into the effects of various grease compositions on jet fuel quality simulating both low and high concentration contamination.

ANALYTICAL METHOD TO DETECT AND CHARACTERIZE ELASTOMERS IN FUEL INSOLUBLES

Thomas N. Loegel, Iwona Leska

Currently there is no standard procedure or analytical method for characterizing fuel gums and sediments to reliably determining whether or not the source of the gum and/or sediment is the result of fuel degradation or the leaching of material from elastomers in fuel system components. This presentation will show the evaluation of multiple analytical techniques for their utility in qualitative analysis of fuel insolubles and the detection of elastomer degradation. Targeted elastomer chemistries used to develop the analytical test methodology included butadiene rubbers, styrene butadiene rubbers, fluorosilicone, silicone, polyurethane, and neoprene. Three analytical techniques; triple-quadrupole mass spectrometer via a solids probe coupled with a corona discharge source, high temperature gas chromatography mass spectrometry (GC-MS) with a pyro-probe thermal desorption interface, and a matrix-assisted laser adsorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) were considered for the analysis of fuel insolubles. Different fuel sample matrix formulations were developed for the detection of elastomer degradation in fuel insolubles. Finally, each method was tested using stressed elastomer products that has been degraded artificially though exposure to elevated temperature, concentrated chemical attack, or UV light exposure to provide more realistic samples. The goal of this research was to provide the means for the end user to determine if a fuel filter failure is due to elastomer or fuel degradation, thus providing for an informed response to future fuel problems.

IMPACT OF DRAG REDUCING AGENTS (DRA) ON GASOLINE DETERGENCY REQUIREMENTS USING ASTM D6201 TEST METHOD

A. Musharah, A.Wedhaya

Drag reducing agents (DRA) have been used extensively around the world to facilitate the transportation of crude oils and refined products, such as gasoline and diesel fuel, by pipeline. These additives, which are mainly composed of polymers of high molecular weights suspended in a dihydrocarbon solvent, mitigate drag by reducing turbulent friction of the fuels in the pipelines, leading to a streamlined flow, and therefore, increasing throughput. The polymer molecular chains that form DRAs are very fragile, and can be sheared or broken by bends in the pipeline, valves, piping branches, and pumps, degrading the DRA’s performance. This degradation can be offset by increasing the DRA dosage or reinjecting additional DRA where significant degradation occurs. However, the concentration of DRA is typically limited in multiproduct pipelines. For jet fuel pipelines, the use of DRA is not permitted in any quantity. A

15ppm limit is often imposed for pipelines carrying motor gasoline as the large DRA molecules can lead to the formation of deposit inside internal combustion engines (ICE), negatively impacting engine performance. One option to overcome this problem is the inclusion of deposit control additives (DCA). This study looks into the possibility of using more DRA to increase pipeline throughput in the presence of an optimum dosage of gasoline deposit control additive. The evaluation was carried out using real engine testing, to understand the impact of using different treatment rates of two drag reducing additives and three deposit control additives. Additive packages are normally composed of various chemicals, hence, the test results could not be linked specifically to a certain criteria. Therefore, the aim of this study was to determine the impact of increasing DRA treatment rate in the presence of different deposit control additives, in addition to identifying the optimum treatment rates of the different combinations of additives. The assessment was performed on gasoline containing 15% MTBE. Drag reducing agents used for this study went through sheering process to mimic real physical conditions after transportation through pipelines. Results suggest that in the presence of an appropriate amount of deposit control additive in gasoline, the concentration of drag reducing agent could be increased without any negative effect on engine performance.

DIESEL EXHAUST FLUID (DEF) CONTAMINATION OF JET FUEL

Mark Rumizen

Two separate events have occurred over the last two years where jet fuel was contaminated with Diesel Exhaust Fluid (DEF) when being uplifted to aircraft from aircraft refueling trucks. These contamination events have received great interest from the U.S. Federal Aviation Administration (FAA), the U.S. military, and the civilian aviation industry due to the severe consequences of this type of fuel contamination. Airport refueling trucks have been equipped with FSII injection systems for many years. These systems require a reservoir mounted on the truck to supply the injection system during aircraft refueling. However, in recent years newer refueling trucks have been introduced with a DEF reservoir in addition to the FSII reservoir. DEF is a urea-based additive used to reduce the NOx emissions of diesel-powered trucks. In the mid-2000's, the U.S. Environmental Protection Agency (EPA) mandated use of exhaust catalysts that required DEF injection for on-road trucks, but this mandate was extended to non-road diesel powered trucks (such as airport refuelers) starting in 2014. Since that time, airport refueling trucks began appearing at airports equipped with two fluid reservoirs to accommodate FSII and DEF. This has created a new risk to safety of flight. DEF is not approved for use in jet fuel and will react with certain jet fuel chemical components to form crystalline deposits in the fuel system. Airplanes involved in the above two incidents experienced clogged fuel filters and fuel nozzle deposits that led to service difficulties and unplanned diversions. This paper will provide background and information that is intended to alert aviation fuel handlers of the risks of DEF fuel contamination and suggest possible preventive measures.

SESSION 3: FUEL ADDITIVES

DESIGNING NO HARMS TESTING FOR DIESEL FUEL ADDITIVES

David J. Evans, Nathan Matheson and Dietmar Posselt

Unlike the aviation industry which is guided by ASTM D4054, diesel fuels lack the framework that provides strict, demonstrated no harms qualification procedures. The aviation fuel additives have oversight by technical authorities, OEMs, as well as fuel experts casting their eyes over technical reports. Whilst the diesel additive OEM has performed extensive evaluations on their products, the information is not distributed which leaves many operators in the dark. This is more evident as commercial/ground distillate market is being further utilised in the marine industry. Currently, the only public accessible diesel additive qualification procedures are the US DOD MIL-PRF-32490 Additive, Lubricity Improver, Distillate Fuel; and the DGMK Report 787 Criteria Catalogue for Additives in Diesel Fuel (lubricity additives and MDFI/WASA) for Refinery Use. These two documents provide an excellent starting point for the establishment of a generic diesel fuel additive qualification guide that covers both ground and maritime applications. This presentation will explore experiences in developing a no harms guide, the difficulties with fragmented product and impact to fit for purpose properties.

HIGH FREQUENCY RECIPROCATING RIG LUBRICITY OF DIESEL FUEL WITH CETANE IMPROVER ADDITIVE

Shouvik Dev, W. Stuart Neill, Jodi Johnston, Ken Mitchell

Diesel fuel lubricates the fuel injection system in compression ignition engines. ASTM Test Method D6079 is a standardized bench test that uses the high-frequency reciprocating rig (HFRR) to evaluate the boundary lubricating properties of diesel fuel. The addition of 2-ethylhexyl nitrate (2-EHN) cetane improver additive (CIA) has been shown to increase the HFRR wear scar diameter (WSD) of some diesel fuels. However, this result is incongruent with pump rig tests conducted with the same diesel fuels. The objective of this research is to investigate the impact of CIAs on HFRR WSD. Lubricity determinations were performed with combinations of No. 1 or No. 2 ultra-low sulphur diesel (ULSD) fuels, ester- or monoacid-type lubricity improver additives (LIAs), and nitrate- or peroxide-type CIAs. Different strategies for modifying the diesel fuel to reduce the WSD were evaluated. The test procedure was also modified to reduce the 2-EHN WSD artifact. When 2-EHN CIA was added to the No. 2 diesel fuel with an appropriate treat rate of ester- or monoacid-type LIA, the HFRR WSD increased by up to 200 μm. However, the addition of 2- EHN CIA to the No. 1 ULSD fuel did not increase the HFRR WSD. The results show that doubling the LIA treat rate or blending 2% biodiesel are two workarounds that reduce the HFRR WSD to acceptable levels. A slight modification to the Test Method that involves ramping up the vibration frequency over a period of time shows potential for minimizing thermal decomposition of 2-EHN during a lubricity determination.

SGS SURVEY 2019: PREMIUM FUELS AND AFTERMARKET ADDITIVES ON THE U.S. MARKET

Dr.Jennifer Schmitt

Petroleum-based fuels have been used for over 100 years. Fuel specifications and engines need to be continuously developed to meet strict regulatory requirements. In the recent years, various components, such as methanol, ethanol, FAME and ether have been used. New developments of blend components e.g. OME or DME are already in the standardization phase. To guarantee a high-quality product, the new components should harmonize well with the existing basic fuel. The use of additives can be advantageous in order to maintain or subsequently influence specific fuel properties. Additives can be added to the fuel either during the refinery process for the production of premium products or by the final consumer using after-market products. In this study we are taking a look at one of the major additive markets - the U.S.. An in-depth analysis of the premium fuel qualities (TOP TIER™) and numerous aftermarket additives was conducted. Therefore, fuels and additives were sampled in different regions within the US and analyzed for their substances and properties. The objective of this study is to evaluate customer behavior, market share, and quality differences of premium fuels. Finally, we are verifying the claims stated on the aftermarket products.

SESSION 4: AVGAS, GASOLINE, DIESEL AND MARINE FUELS

APPLICATION OF TWO-DIMENSIONAL GCXGC TECHNOLOGY FOR AVGAS OXIDATION RESEARCH

Cunping Huang and Sneha Gollamudi

The oxidation stability of aviation gasolines (Avgas) is an issue for the maintenance of all types of combustion engines. An avgas can contain multiple hydrocarbon types and additives. Avgas oxidation behavior can be complex. The identification of low concentration intermediates and final products of fuel oxidation can be an especially great challenge. Two-dimensional chromatography is currently a state-of-the-art technology. Since its invention it has found application in complex aviation fuels analyses. GCxGC chromatography is a powerful chromatographic technology that provides sensitive and effective separations for complex mixtures that are not possible by conventional one-dimensional gas chromatography. In this research we have used a typical 100 low lead (100LL) aviation gasoline as an example for the basic understanding of a fuel’s oxidation process and the identification of its final products. For detailed hydrocarbon analyses high resolution and high sensitivity comprehensive two-dimensional gas chromatography/time of flight mass spectrometry (GCxGC/TOFMS) were used to determine a low-level fuel’s oxidation intermediates and products. The concentrations of fuel oxidation products were measured using GCxGC/FID (Flame Ionization Detector) analyses. To better characterize the formation of a fuel oxidation functional group, a high sensitivity FT-IR spectrometer was used to observe C=O and C-O- functional groups during oxidation. Analyses of a fuel’s physical and chemical properties before and after fuel oxidation, such as fuel net heat of combustion, viscosity and vapor pressure, were also carried out based on related ASTM standards in order to investigate the effects of fuel oxidation. The results indicate that fuel oxidation can cause a degradation of tetraethyllead (TEL), the primary octane booster for 100LL

aviation gasoline, the effects of which are not well understood. The research findings will inform the understanding of the oxidation stability of unleaded aviation gasolines as well.

EVALUATION OF PARTICLE FORMATION TENDENCIES OF MARKET GASOLINE FUELS –IMPACT OF HIGH BOILING COMPONENTS AND AROMATICS

Arij Ben Amara, Toni Tahtouh, Laurie Starck

The reduction of particulate emissions is amongst the most important challenges facing the development of future gasoline engines especially with the increasing concern about Real Driving Emissions and the need to limit the vehicle environmental impact throughout its life service. However, this requirement is dependent not only on the vehicle technology but also on the quality of the market fuel employed. In fact, market fuels may present a wide variation range of physical and chemical characteristics that can significantly impact particles emissions. More particularly the influence of high boiling point components and heavy aromatics on particles emissions was highlighted in several literature works. Although several theoretical studies addressed the impact of aromatics structure on particles formation, the correlation between aromatics structure in market gasoline fuels and particles emissions remains poorly understood. The objective of this work is firstly, to investigate the relationship between particulate matter emissions and gasoline fuel composition with a special focus on aromatic structure and secondly, to assess the sensibility of several Particles Matter Indices. To achieve this, a fuel matrix composed of commercially available and laboratory formulated gasoline fuels was built presenting a wide variation of aromatics content and structure. The fuel matrix was characterized using the association of several techniques including Detailed Chemical Analysis by Gas Chromatography (GC), distillation, Dry Vapour Pressure Equivalent, Octane Number and Gums. Besides, the fuel tendency to particles emissions was characterized using laboratory test including the Smoke Point (ASTM D1322) as well as vehicle homologation tests on the Worldwide harmonized Light vehicles Test Cycles (WLTC) and the New European Driving Cycle (NEDC). Results reveal a different sensitivity of the PM indices to fuel composition especially aromatic content and structure. The comparison of PM index with original data of SP as well as vehicle emissions allowed a critical analysis of the real impact of aromatics on sooting tendency and a new insight into the development of representative knowledge-based Particulate Matter Indices for market gasoline fuels.

THE ISRAELI PROGRAM OF M15

Amiram Groweiss

Several years ago, the Ministry of Energy, Water and Infrastructure in Israel, has commenced and promoted a program for the use of M15, a blend of 15% methanol and 85% EN-228 gasoline as a fuel for vehicles, especially for passenger cars. The rationale for this program stemmed from the large reservoirs of natural gas, ca. 1000 BCM, that were discovered near the Israeli shores in the Eastern Mediterranean. The research and demonstration programs were carried out by collaboration between the Ministry, researchers from the Academia, the Standard Institution of Israel and Dor Chemicals Ltd., a privately owned company, who – at certain times – were a

manufacturer and importer of methanol in Israel. The program raised interests in several parts of the world like in China, India and by the Italian automaker Fiat. The program included, among alia, road tests of twelve cars, which lasted several years, including a thorough investigation of the car motors at accredited laboratory after completion of the road tests. Another study dealt with the exhaust emissions of cars driven on M15 and M56, with comparison to RON 95, and in another study, the compatibility of elastomers and polymers used in vehicle fuel systems with M15 and other similar fuels. Finally, the SII (Standard Institution of Israel) has approved standard IS 90-4 for M15. That standard does not differ much from the European Standard EN-228 (except for the percentage of oxygen and oxygenates) but gives a relaxation on the problematic issue of vapor pressure. All those subjects will be discussed and discussed briefly in this presentation.

COMPARISON OF THE INNOSPEC LOW TEMPERATURE OPERABILITY RIG TO COMMON LOW TEMPERATURE OPERABILITY ESTIMATION METHODS

Alex Belly

Since the proliferation of ultra-fine filtration (UFF) of diesel fuels, there has been an increase in field issues surrounding bulk fuel filtration. It would be expected that modern vehicle fuel filtration may also experience similar increases in field issues as filter porosities decrease. Commonly used Low Temperature Operability (LTO) methods, such as Cold Filter Plugging Point (CFPP) and Low Temperature Flow Test (LTFT), were originally correlated to vehicle fuel filters used over 30 years ago. At that time, vehicle fuel filters were as large as 130 µm. Today's modern vehicle fuel filters can have primary filtration of 10 µm with secondary filtration down to 2 µm. Previous research in Innospec's Low Temperature Operability Rig (LTOR) found that under the same test conditions, fuel filterability performance varied among different filter media. This paper raises concerns about current LTO estimation methods and their applicability with modern UFF media. To investigate this, three similar UFF filter media were tested in Innospec's LTOR. The findings generated from the LTOR data cast doubt on the reliability of widely used methods to predict LTO in modern fuel systems utilizing UFF.

USING SPECTROSCOPIC ELLIPSOMETRY TO NORMALIZE DIESEL INJECTOR FOULING EVALUATION

George R. Wilson, III, Steve Westbrook, Doug Yost, John Gomez

A new test methodology was developed under a recent program funded by the Coordinating Research Council (CRC). The test involves an injector test rig based on a rig developed by a fuel injection equipment company. A primary purpose of this program was to determine if the use of spectroscopic ellipsometry, to quantify injector pintle deposits, would allow a significant reduction in the levels of contaminants and additives, used in the test fuel, compared to amounts used in other testing. This paper presents some of the results from the CRC project. It also discusses how using a far more sensitive analytical technique resulted in a performance test that was shorter, less expensive, more realistic, and more sensitive.

OPTIONS FOR MEETING IMO 2020 COMPLIANT FUEL

Joseph Stark, Kevin Cote

In accordance with MARPOL Annex VI, on 1 January 2020 the sulfur content of fuel oil used on board commercial ships trading outside Emission Control Areas (ECAs) must not exceed 0.50% m/m. The 0.50% sulfur limit is a significant reduction from the current global limit of 3.50% m/m which has been in place since 2012. The worldwide implementation of this important new International Maritime Organization (IMO) requirement – referred to in this guidance as the 'Global Sulfur Cap' – therefore represents a regulatory game changer that will have global impact on the refinery and shipping industries. Ships switching from non-compliant fuel to IMO 2020 compliant fuel will need to address the residual high sulfur containing fuel that exists in tanks before the 1 January 2020 deadline. As compliant fuel used to meet the 0.5% sulfur cap is not readily available, as of the writing of this abstract, there are limited options for ship owners to meet the new regulation. Ship specific implementation plans will need to consider when and where any new 0.5% S max fuels will be bunkered and the designated tanks into which they will be loaded. Ship owners and operators will need to decide between cleaning tanks designated for the bunkering of compliant fuel or loading compliant fuel into designated tanks on top of the remnants of 3.5% S max fuel as part of a dilution/flushing process. Complete turnover timelines must be started early enough to allow an appropriate period of time before 1 January 2020 to ensure all non-compliant fuel is out of the system before this date. This process should be carried out carefully keeping in mind the possible associated risks resulting from incompatibility between the two fuel grades. The option to clean tanks designated for bunkering of compliant fuel allows for complete removal of any high sulfur containing residue and assurance of avoiding any penalties for ship owners for not being in compliance. A tank cleaning strategy will help to mitigate the possibility of blending incompatible high sulfur heavy fuel oil (HFO) with IMO 2020 compliant fuel oil (VLSHFO) and can be completed relatively quick without having to burn through a flushing process to turn over fuel tanks.

SESSION 5: THERMAL STABILITY

THE ROLE OF SURFACE COMPOSITION IN ULSD THERMAL DEPOSITION

David J Abdallah, Krystal B. Wrigley, Ryan C. Kerfoot

The effect of fuel system metallurgy on fuel stability is an important concern in the development of high efficiency/advanced engine technology. Surface composition in the fuel system could dramatically effect processes such as fuel oxidation and deposit adherence. Depending on the coatings, fuel deposition can be accelerated by instigating fuel degradation or resistant by concealing the physiochemical aspects of the surfaces. Here we look at the impact of a variety of surface coatings on the thermal stability of a single diesel reference fuel. Results reflect that surface composition has a significant effect on the mechanism of fuel deposition. Differences in deposit onset reflect differences in surface activity and are used to rank the various surface compositions on their ability to accelerate fuel degradation. The surface composition was found not only to change the breakpoint temperature but the level and profile of fuel deposition. More importantly, this work advances our understanding of the correlation of fuel wetted surface to fuel thermal deposition which is a concern in the development of high efficiency engines.

UNINTENDED CONSEQUENCES OF THERMALLY ACCELERATED FUEL STABILITY TESTS

Robert E. Morris, Kristina M. Myers, Thomas N. Loegel

Laboratory testing has traditionally been employed to validate the fit for purpose of a mobility fuel, and stability is an important performance metric. When selecting appropriate test methods, the analyst must choose between a direct test or simulation, and a laboratory test that is somehow linked to the fuel characteristic of interest. Thermal and storage stability testing typically relies on thermal stressing to obtain test results within a reasonable timeframe. These accelerated laboratory tests have historically been developed around the assumption that reaction rates, and hence the fuel property related to the relevant chemical reaction pathways, will increase at the same rate for all fuels with temperature. The basis for this assumption has been the Arrhenius relationship, which implies that a rate of a chemical reaction will double for each ten degree increase in temperature. However, the Arrhenius equation expresses the relationship between reaction rate and temperature of a single first order reaction. Complex organic systems, such as fuels, react through a series of complex of reaction activation energy profiles that change with temperature to initiate a series of parallel and sequential reaction mechanisms. As a consequence, there is an often ignored or misunderstood risk inherent in any thermally accelerated test, particularly when it involves a system as complex as mobility fuel. The impact of this can be seen in the disconnects between different stability test results, and situations where reactive fuels fail specification accelerated stability testing, but are found to be stable in use. The risks inherent in thermally accelerated fuel stability testing will be illustrated by examination of the kinetics of complex chemical systems with several known key fuel autoxidation reaction mechanisms.

GAINING A DETAILED UNDERSTANDING OF FUEL DEPOSIT FORMATION MECHANISMS THROUGH ADVANCED MOLECULAR AND SUPRAMOLECULAR CHARACTERIZATIONS

Charlotte POURTIER, Perrine COLOGON, Thibaud CHEVALIER, Mickaël MATRAT, Loïc BARRE

Fuels stability towards oxidation, especially the formation of insoluble deposits that may compromise the engine operation, is currently one of the major challenges faced by the transport industry (automotive and aeronautic). Contrary to conventional approaches studying deposit formation from a macroscopic perspective (thickness, speed of growth …), the aim of this work was to carry out a thorough analytical study both at molecular and supramolecular scale by using complementary and cutting-edge techniques such as gas chromatography coupled to mass spectrometry, low- field 1H NMR, FTIR and Small-Angle X-Ray Scattering. Two surrogate compounds contributing significantly to jet fuel formulation were selected: N- octane and toluene, for alkanes and aromatics respectively. Samples were oxidized in an autoclave (160°C, 7 bar O2) with sampling at different oxidation levels, followed by deep analysis. Samples exhibited very different phase behavior: toluene autoxidation led to the generation of an insoluble deposit and octane autoxidation resulted in liquid-liquid phase separation. Although such observations were already reported in the literature, their detailed understanding still

remains unclear and most studies are limited to the analysis of the main phase. Therefore, specific protocols for phase isolation were developed and partitioning of compounds was investigated. One major result was the identification for the first time of two molecules present in toluene deposit, including 2,5-furandione. The early presence of this molecule was evidenced in oxidized samples and confirmed by analysis of a standard. This highlights the essential role played by oxygenated compounds in deposit formation and enables to propose a model for deposit structure.

STUDIES OF THE IMPACT OF FUEL DEOXYGENATION ON THE FORMATION OF AUTOXIDATIVE DEPOSITS

Steven Zabarnick, Zachary J. West, Amanda Arts, Milissa Griesenbrock, Paul Wrzesinski

The formation of gums and surface deposits in aircraft fuel systems is known to be caused by oxidative reactions which occur at elevated temperatures as jet fuel is used as a coolant or by passive heating during passage through hot engine sections. In recent years a number of organizations have proposed and developed in-line aircraft fuel deoxygenation systems to reduce the dissolved oxygen content with the intent of reducing detrimental products from these oxidative processes. The cost and weight penalties associated with installing such systems means that it is essential that fuel deoxygenation be evaluated for its efficacy over a range of aircraft fuel operating conditions. In this work we explore the effect of fuel deoxygenation levels on oxidation processes and autoxidative surface deposit formation via experimental and modeling approaches. Experimental measurements of oxygen consumption and deposition are performed over a range of initial oxygen levels in the Near-Isothermal Flowing Test Rig heated tube rig and Quartz Crystal Microbalance systems. In addition, computational fluid dynamic computations which include an autoxidative chemistry chemical kinetic mechanism are used to help understand the effect of deoxygenation at partial and complete oxygen consumption conditions. The results indicate that under partial oxygen consumption conditions (e.g., high flows and low temperature), such as are usually present in aircraft fuel systems, deoxygenation systems may have significantly reduced effectiveness in eliminating deposit formation. Conversely, during complete oxygen consumption conditions (low flows and high temperature) deoxygenation can be very effective. The results show the complex effect of fuel deoxygenation and point to the need for careful analysis of fuel deoxygenation systems efficacy at actual aircraft fuel system operation conditions.

INVESTIGATING THE EFFECT OF FLUID DYNAMICS ON THE FUEL AUTOXIDATION PROCESS

Diego Marco-Garcia, Simon G. Blakey, Mark Simmons, Richard Greenwood

Fuel is used in modern aircrafts as a heat sink before it is burned in the combustor. With constant performance engine improvement as the main target, the temperature at which the fuel is exposed is nothing but rising. Because of this increase of thermal stress, not only the properties of the fuel but also the life of the fuel system might be hindered. Historically, the chemical aspect of fuel thermal degradation has been widely studied; however, it is important to remember that the final deposition rate is a combination of a chemical and a transport process. The fluid

dynamics state of the fuel inside the fuel pipes dictates the transport of the chemical compounds towards the different pipes areas. In order to further understand the combined effect of chemistry and fluid dynamics a series of experiments has been carried out in two standardised thermal stability rigs for both, laminar and turbulent flow. The data collected has been used to validate a pseudo-empirical model that tries to combine the chemical aspects of deposition together with the flow condition in order to predict deposit formation rates. Finally, an improved chemical kinetic model will be implemented in FLUENT to validate both the accuracy of the experimental results and the predictive capabilities of the pseudo empirical chemical-fluid dynamic deposition model.

THE EFFECT OF VARIATION IN SI/AL RATIO OF ZEOLITE ON AVIATION FUEL THERMAL STABILITY IMPROVEMENT

Ehsan Alborzi, Simon G. Blakey

Gas turbine fuels are exposed to thermal load en-route from the fuel tank to the combustion chamber, through the engine fuel supply system. The increasing temperature of fuel as it passes through the engine fuel supply system, initiates a multitude of chemical reaction in bulk fuel. This results in the formation of numerous soluble and insoluble complex organic molecules, composed of hydrocarbons, sulfur, nitrogen and oxygen. These species ultimately contribute to the formation of carbonaceous deposits on the surface of the fuel system. In theory, removing dissolved molecular oxygen can improve the stability of aviation fuels. However, it has been reported that the impact of fuel deoxygenation on surface deposition depends on the distribution of trace sulfur and nitrogen containing molecules as well as oxygenated species.1,2,3,4 Zeolites have been used as solid adsorbents for partial fuel deoxygenation 5 and polar species removal in the lab scale applications. 6 Zeolites exhibit both physisorption and chemisorption behaviour in interactions with guest molecules. It is hypothesised that the interaction of polar species with zeolites is controlled by strong electrostatic field on the internal surface of zeolite due to the presence of alumina. This article presents the experimental study of the effect of variation in Si/Al ratio of zeolite 3.7 A on the improvement of thermal stability of a Jet A-1 fuel type in a lab scale application. The experimental findings prove a strong adsorption of oxygenated species, dissolved metals (Fe) by zeolites which in turn indicate a substantial enhancement in fuel thermal stability.

JETSCREEN PROGRAM: HIGHLIGHT THE IMPACT OF THE JET FUEL CHEMICAL COMPOSITION ON THERMAL STABILITY BEHAVIOR

Mickaël Sicard, Maira Alves Fortunato, Simon Blakey, Ehsan Alborzi, Syeed Yoousof Sadat, Laurie Starck, Benjamin Veyrat, Livio Neocel, Axelle Baroni

The study of the potential of a fuel to form surface deposits is an important topic in the overall qualification procedure of a fuel. Particularly the trace components of Sulfur in the fuel. The objective of that study, done within the framework of the European program JETSCREEN, is to highlight the impact of the Sulfur content and aromatics on the thermal stability behavior of fuels. Three fuels were used: a Jet A-1 and two extreme fuels: high aromatic and zero-aromatic. The varying Sulfur levels of the fuel were achieved by a process of successive hydrotreating of

the fuel to achieve higher quality thermal stability behavior. A range of testing was carried out in the programme on a number of different scales. At IFPEN, testing was carried out using the Petroxy device and the pressure drop caused by the consumption of headspace oxygen was recorded. At ONERA, the Reflux condenser device was used and the liquid and gaseous phase of the device was analyzed at number of different time periods to produce validation data on the likely reaction chemistry associated with each fuel. The ONERA coking test bench also produced cyclic testing of fuel in a simulated fuel injector system. At USFD, tests using the JFTOT with surface interferometry and the HiReTS rig were conducted. As a whole, the results from these different rigs present a useful validation set of data for the development of more robust chemical kinetic models of deposition at a range of scales.

DEVELOPMENT OF A THERMAL STABILITY REFERENCE FLUID

Zachary J. West, Susan S. Mueller, and Steven Zabarnick

Assurance of aviation turbine fuel thermal stability is a necessary check for today's modern aircraft. While many methods exist to examine jet fuel thermal stability, the only allowed method for assessing jet fuel thermal stability—for most internationally recognized jet fuel specifications—is ASTM D3241. A confluence of recent events, such as: introduction of metrological methods of heater tube rating, reported variations between D3241 instrument versions, and observed variability of D3241 results during the ASTM Interlaboratory Crosscheck Program, has given rise to a desire for a means of verifying the test equipment used for thermal stability evaluation. In an effort to improve thermal stability evaluations, we report on our process to develop a robust and consistent thermal stability reference fluid. Results and interpretation of deposition and differential pressure will be reported for various candidate fluids.

SESSION 6: DATA ANALYTICS AND MODEL DEVELOPMENTS

APPLICATIONS AND ASSESSMENT OF DATA ANALYTICS SYSTEM FOR FUEL COMPOSITIONAL DATA

Andy M McDaniel, Sean Fischer, Alison E. Metz, Jeffrey Cramer, Richard A. Kamin, Michelle Klem

As methods for reporting detailed bulk and trace fuel composition information are being implemented across the DoD, the U.S. Navy is designing and implementing a dedicated data analysis system to utilize these high volumes of increasingly complex fuel data. This paper presents the Navy's research and development in data analytics technology to evolve approaches to increase its understanding through chemical composition datasets. This paper will summarize the data system architecture and best practices utilized to develop the data schema and data cleansing algorithms. Case study results will be presented to illustrate the analytics system's potential to provide deeper understanding of the role of fuel composition in problem identification and resolution. Within these case studies, conventional data techniques are compared to various modern machine learning techniques, and the benefits of shortcomings of

each technique are analyzed. This paper concludes by assessing future roles of data analytics technology in aviation and diesel fuel user communities.

MACHINE LEARNING ALGORITHMS FOR FUEL PROPERTY PREDICTION IN COMPARISON WITH STATE OF THE ART PHYSICAL MODELS

Clemens Hall, Bastian Rauch, Uwe Bauder, Patrick Le Clercq, Manfred Aigner

A reliable way to accurately predict the properties of fuels is essential to ensure their effective utilization. Furthermore, this could facilitate the development of alternative fuels and help to streamline their approval process. This work investigates the application possibilities of Machine Learning (ML) algorithms for the prediction of jet fuel properties. A critical evaluation is performed by comparing ML-based property predictions with state-of–the-art physical-based models. A sub-set of properties from ASTM D1655 Table 1 was selected for this study. The detailed fuel data set from the CRC world fuel survey (CRC Report No. 647, June 2006 CRC, INC.) was used as the basic data set to represent the variability of conventional fuel properties. The detailed compositional information was then correlated with the target properties by using different ML algorithms. The prediction via ML was carried out by pre-processing the data, selecting suitable features and performing the regression with several parameter optimized algorithms. The validity of the predicted values was cross-validated in 4 folds with 25 % percent of test data. Furthermore, the possibility of directly correlating and predicting fuel properties based on other fuel properties with ML was examined. Established physical models, based on measured thermodynamic constants or derived from group- contribution methods, were given the same detailed compositional information as the ML algorithms, and then used to predict the chosen fuel properties. Finally, the two approaches were tested and compared with respect to their accuracy in the validated / trained data range and also their extrapolation behaviour. The applicability of ML for the purpose of fuel property prediction was then analysed.

JETSCREEN PROGRAM: QUANTITATIVE ASSESSMENT OF THE JET FUEL PHYSICAL, CHEMICAL AND THERMOPHYSICAL PROPERTIES AND DEVELOPMENT OF LOW AND HIGH FIDELITY MODELS

Maira Alves Fortunato, Laurie Starck, Martha Hajiw-Riberaud, Benoit Creton, Yanis Melliti, Jacques Ancelle, Frédéric Ser, Mickaël Sicard, Uwe Bauder, Bastian Rauch, Patrick Le Clercq

The present work was made within the framework of the European project JETSCREEN. We have elaborated models to describe with very high accuracy basic physico-chemical properties such as density, dynamic viscosity, net heat of combustion, distillation curve and specific heat, suitable for alternative aviation fuels. The work was divided in two main parts: an experimental part where the physical, chemical and thermophysical properties of jet fuels were investigated to give the quantitative assessment necessary to develop high predictive models. A second part where these data were used to access variations in fuel composition and to build fuel sensitive thermophysical models and chemical reaction kinetics models. The present paper focuses on experimental data obtained at IFPEN and ONERA as well as the development and validation of the different models at ONERA, DLR and IFPEN. The fuel matrix was composed of a commercial Jet A-1, alternative fuels as ATJ-SPK as well as extreme fuels one with high

aromatic content and another with zero-aromatic content. At IFPEN, the detailed chemical composition analysis was obtained by means of GCxGC. At ONERA, the main physical chemical properties were measured such as density, dynamic viscosity, net heat of combustion, distillation curve and specific heat. Also, at ONERA low fidelity models were developed suitable to describe these properties. The models were then tested and validated on the experimental measurements. High fidelity models were also selected/developed and validated against the experimental data.

SESSION 7: FUEL MICROBIOLOGY

A REVIEW OF LATEST INDUSTRY GUIDANCE ON ANTI-MICROBIAL STRATEGIES FOR DISTILLATE FUELS

Graham C. Hill

In 1994 Edward Hill presented an overview of "Safe, acceptable anti-microbial strategies for distillate fuels" at IASH in Rotterdam. The intervening 25 years has seen considerable changes in fuel chemistry, the widespread introduction of biofuels and synthetic fuels, regulation restricting the availability and use of biocidal chemicals, and a host of new industry best practice documents. It therefore seems timely to review the strategies available for control of the potentially severe impacts of microbial growth in liquid fuels. This review paper considers the options for prevention and treatment of microbial growth in fuel systems including, routine maintenance procedures, tank and system design, filtration and other particulate removal equipment, product settling, physical cleaning, and use of biocides. It stresses the importance of a holistic approach in controlling microbial growth, from refinery through to fuel end use and it outlines the strategies for monitoring and validation of anti- microbial measures with latest test technology. The paper also provides an overview of the recently published industry guidance and resources to enable implementation of best practice. This paper is dedicated to the memory of Edward C. Hill. and his invaluable contribution to fuels microbiology.

PEPTIDE-BASED BIOSENSING FOR RAPID DETECTION OF FUEL BIOCONTAMINANTS

Oscar N. Ruiz, Thusitha S. Gunasekera, Osman Radwan

Microbiological contamination can affect the quality and properties of fuel, and the operation of fuel systems. Adverse effects of biofouling include filter clogging, fuel emulsification, malfunction of fuel/water separators, biocorrosion, coating degradation, and fuel quality changes. Thus, it is critical to develop simple and quantitative methods for early detection of biocontamination in fuel. Here we describe the development, use and validation of a microbial detection assay based on broad-range peptide biorecognition elements (BREs) conjugated to quantum dots (qdot) for detection of microorganisms in fuel by measuring fluorescence. Phage-display in the presence of fuel was used to isolate heptameric peptides capable of binding to conserved cell surface determinants of fuel-degrading bacteria and fungi discovered via functional genomics and transcriptomics. Peptide-functionalized qdots were used as signal

transducers for rapid detection and quantification of microbes. The peptide-qdot chemistry is being applied through a fuel lateral assay to provide rapid fluorescence-based detection of microbes in fuel. We are currently researching the biofunctionalization of optical and electrical transducers with peptide BREs for development of real-time biosensors for fuel applications.

THE RELATIONSHIP MICROBIAL COMMUNITY VITALITY AND ATP BIOBURDEN IN BOTTOMS WATERS UNDER FUEL MICROCOSMS

Frederick J. Passman, PhD, Jordan Schmidt, PhD, Russell P. Lewis, and Perry Christian, PhD

Adenylate energy charge (AEC) – computed from the adenosine triphosphate (ATP), adenosine diphosphate (ADP), and adenosine monophosphate (AMP) concentrations in a specimen reflect the net physiological state of the microbial population in that specimen. Previous research has demonstrated that healthy microbial populations maintain AEC $\geq$ 0.8. As populations are subjected to stresses, or – in closed systems – deplete the available nutrients, respond to the accumulation of toxic metabolites, or both – AEC decreases (often to <0.5). Aqueous-phase samples from a set of fuel-water microcosms were tested for cellular ATP (cATP) and AEC. This paper reports on the precision of the AEC test method and the relationship between cellular AEC and cATP-bioburdens in the aqueous-phase of fuel over aqueous-phase microcosms.

THE RELATIONSHIP BETWEEN PLANKTONIC AND SESSILE MIROBIAL POPULATION ADENOSINE TRIPHOSPHATE BIOBURDENS IN DIESEL FUEL MICROCOSMS

Frederick J. Passman, PhD, Jordan Schmidt, PhD, Russell P. Lewis, and Perry Christian. PhD

Fluid samples drawn from the fuel, interface and water phases of fuel over water microcosms were tested for cellular Adenosine triphosphate (cATP). Additionally, surface swab samples from steel corrosion coupon surfaces exposed to each of these three phases were collected and tested for total ATP (tATP). Relationships between planktonic and sessile population ATP concentrations were determined, as were relationships among ATP bioburdens in each of the three listed microcosm phases. This paper describes the relationship between planktonic and biofilm population ATP bioburdens in: 1) the bottoms-water, 2) interface, 3) fuel phases, and 4) biofilms of the tested steel coupons; the relationships among planktonic ATP-bioburdens in each fluid phase and the relationship among biofilm bioburdens on each corrosion coupon zone.

DEVELOPMENT OF qPCR-BASED DETECTION AND QUANTIFICATION OF FUNGAL CONTAMINATION IN FUEL SYSTEMS

Yakir Ophir, Moshe Rabaev, Rami Nechooshtan, Idan Hefetz, Joseph Geva, Raphael Fass, Yehuda Sapir, Haim Yehuda, Liel Mazar

The routine microbiological monitoring of Jet fuel is one of the most important risk assessment QC measures for aviation fuel supply facilities and aircraft fuel tanks. The laboratory of environmental microbiology and biotechnology at IIBR, provides the Israeli Air Force continuous microbial monitoring and control of fuel systems. The monitoring allows early

detection and risk assessment, predicting the likelihood of problems developing and addressing existing damage before it becomes unmanageable. The monitoring program implements for the last two decades the laboratory reference method conventional microbiological technique, ASTM D6974 / IP 385 "filtration and culture procedures" recommended by the JIG guidance. Based on many years of experience gained in microbial monitoring of fuel systems it became obvious that the majority of biomass fouling fuel tanks and filters is due to fungal species. As a part of an effort to develop a sensitive, rapid, reliable detection and quantification assay, the development of qPCR protocol to detect and quantify the total fungal contamination of fuel systems is reported here. Two primer sets, targeting the 18S and 28S rRNA fungal genes were selected. Applying the primers in the established qPCR protocol validated their ability to amplify, detect and quantify all fungal and yeast strains isolated from Jet Fuel. Evaluation of the qPCR protocol developed in a comparative investigation of real life "field samples" showed high degree of correlation between levels of fuel-phase fungal contamination determined by ASTM D6974 and those received by qPCR that was developed.

THE EFFECT OF TEMPERATURE AND TIME INTERVAL PRIOR TO TESTING ON THE DETECTION OF MICROORGANISMS IN FUEL SAMPLES

Gareth J. Williams, Leon P. O'Malley, Nathan G. George, Graham C. Hill

Ideally, samples for microbiological analysis should be tested as soon as possible after being drawn. If fuel samples are to be returned to a laboratory or other facility for microbiological analysis, and there is significant delay before testing, it is likely that the results may under- or overestimate the level of microbial contamination present at the time of sampling. After fuel samples have been drawn, microorganisms present in the samples may slowly die with time. Conversely, if samples contain free water this may facilitate the growth of microorganisms. Industry guidance documents recommend that microbiological testing should be conducted on samples as soon as possible and ideally within 24 or 48 hours of them being drawn. ASTM D7464 Standard Practice for Manual Sampling of Liquid Fuels, Associated Materials and Fuel System Components for Microbiological Testing stipulates that unless samples can be tested within 4 hours they should be refrigerated during transportation. Many of the studies conducted in relation to changes which may occur in microbial populations in samples during transit, relate to aqueous samples. To our knowledge, few, if any, published studies investigate time and temperature during transit and storage on fuel samples prior to microbiological analysis. This paper reports an investigation of the effect of time interval prior to testing and temperature on the recovery of microorganisms by industry standard methods from field samples of automotive diesel, gas oil and aviation fuel.

SESSION 8: AVIATION FUELS

IMPACT OF SOX EXPOSURE ON RESPONSE OF JET FUEL TO STATIC DISSIPATOR ADDITIVE

Paul P. Wells

Jet fuel shipped via water often responds poorly to the addition of static dissipator additive (SDA) at the receiving location. The headspace of marine vessel compartments is usually inerted via the addition of scrubbed exhaust gas from an inert gas system (IGS). A malfunctioning or poorly maintained IGS may expose the jet fuel to higher than normal levels of sulfur oxides (SOX) as well as other contaminants like particulate matter. The exposure to SOX in particular is theorized to cause poor response to SDA. The impact of SOX exposure on the response of jet fuel to SDA in a laboratory setting is explored. Research has been conducted using both a SO3 compound and gaseous SO2. Methods to mitigate jet fuel exposure such as water washing and clay treatment are evaluated.

COMMERCIAL DEVELOPMENT AND DEPLOYMENT OF SUSTAINABLE ALTERNATIVE JET FUEL

Mark Rumizen

Since 2006, the Commercial Aviation Alternative Fuels Initiative (CAAFI) has sought to enhance energy security and environmental sustainability for aviation through the use of sustainable alternative jet fuels (SAJFs). CAAFI is a coalition of airlines, aircraft and engine manufacturers, energy producers, researchers, international participants and U.S. government agencies. Together these stakeholders are leading the development and deployment of SAJFs for commercial aviation. CAAFI's goal is to promote the development of sustainable alternative jet fuel options that offer equivalent safety and favorable costs compared with petroleum based jet fuel, while offering environmental improvement and energy supply security for aviation. CAAFI pursues a set of key priorities to enable the success of SAJF deployment. CAAFI's priorities are to: Grow the sustainable AJF supply by developing, optimizing, and aligning feedstock, production, and end user resources that ultimately lead to commercial deployment; facilitate the approval process that enables commercial aircraft to operate with sustainable alternative jet fuel; Communicate the benefits of sustainable AJF; Develop and publish guidance material, best practices, and other documents as resources for stakeholders in the sustainable AJF supply chain. This paper will review the evolution and growth of the sustainable AJF supply chain over the last decade through a discussion of the validation of the use of sustainable AJF through examples of commercial airline and military usage in operational demonstrations and in regular service; progress in the sustainable AJF fuel approval process leading to the availability of fuels produced from six different conversion pathways that have supported the above operational experience; the growth of sustainable AJF supply through an overview of existing and planned production facilities; the commercial agreements for future production and supply of sustainable AJF that highlights the market viability of these fuels; government grants and other financial vehicles intended to promote the use of sustainable AJF to help meet carbon emission goals and mandates.

ADVANCED FUEL PROPERTY DATA PLATFORM: OVERVIEW AND POTENTIAL APPLICATIONS

Simon Blakey, Bastian Rauch, Anna Oldani, Tonghun Lee

This report outlines the establishment of an advanced database for management and integration of current and future aviation fuels. Fuel property and performance data has been gathered for many years in public and company specific fuel surveys. These surveys are suitable for quality control information and for monitoring changes and trends in fuels used for flight. Significant data has been generated for alternative fuels as part of their approval through ASTM D4054. Recently, the experience of this data has led to the development of the Fast Track route for fuels approval, when the fuel is constrained to a necessarily narrowly defined composition. The data behind these developments are often stored in an unindexed way, resulting in their underutilisation for a range of research, engineering design, specification, and in service quality control applications. To make best use of this data, we present a flexiable format for the storing of fuels data. This concept has been proposed by the European H2020 JETSCREEN project in conjunction with the US FAA Center of Excellence, ASCENT programme. We have worked collaboratively to develop a database which currently contains data from around 30,000 conventional and 400 alternative fuels/fuel blends from a range of European and US lead research programmes and data sources. We present test cases for how this model for data storage could be used for the benefit of all. We invite further suggestions for the use of this approach and welcome opportunities to work with the wider fuels community to develop this idea further.

SESSION 9 - SECTION 1: FUEL TESTING AND TEST METHODS

THE DEVELOPMENT AND USE OF 2 µm PARTICLE COUNTING INSTRUMENTS IN FLUID POWER SYSTEMS

Matt Fielder and Steve Georgii

It is recognised and well documented that fluid contamination is the primary source of hydraulic system failure. Solids, water, microbial, incorrect oils/fuel/fluids, aeration, over pressurisation, cavitation, poor selection of filtration, no filtration, aged/oxidised fluids, wrong viscosity, poor conductivity, high acid number and moisture all effect what is the life blood of a hydraulic circuit. The methods by which we monitor and check the condition of the fluids used have become a staple of the Condition Monitoring mantra that we all mostly practice. Particle Counting is now a long- and well-established technique for determining fluid cleanliness in Hydraulic fluids and growing in acceptance in Fuels. However, the limits of its performance in detecting and counting the low range of particle sizes, especially for use online and in the field, are being questioned, and possibly masking the common assumption that “if we can’t see it, it’s not a problem!” by many. This paper/presentation looks at the efforts to extend the size range below 4 micron (c) whilst maintaining recognised calibration standards through the use of hybrid particle counting technologies combined into usable, small, cost effect field based instruments.

1987 saw the last big step change in the particle counting world with the introduction of >4, >6 and >14 micron (c). Does the demand for improved productivity, efficiency, performance and ultimately fluid cleanliness require better in field particle counting resolution?

NEW HANDHELD BIOFUEL IN FUEL METHODS, AN APPRAISAL

Paul Spitteler

Added bio or alternative components like FAME and ethanol to conventional fuels have become a reality all over the world. Fuel properties are dependent on bio content and in a lot of countries there are regulatory requirements for the added components. It is therefore imperative their content can be checked. Laboratory measurement methods are well known and used, but hand-held methods add a level of convenience and speed. A study was done to compare handheld with various laboratory methods showing that precision can compare very favourably to the lab-based systems and that the smaller size is not necessarily a trade-off for performance.

ADVANCES IN THE QUANTITATIVE SPECIATION OF PETROLEUM HEAVY ENDS

H. Muller, N.A. Alawani, F.M. Adam, S.K. Panda, Q. Saleem, E.A. Al-Alawi, A.H. Al-Saleh

The development, optimization, and integration of technologies for refining, distribution, and petrochemical processes hinges on the availability of data for the targeted feedstock and product slates. Ideally, tailoring processes to the exact chemical composition requires quantitative knowledge of feedstocks, intermediates, and products, as well as their chemical transformations, at the level of individual molecules. The quantitative speciation of light and middle distillates has become routine over the last decades. In contrast, high- and non-boiling petroleum fractions (“heavy ends”) can be assessed only qualitatively at near-molecular detail; a quantitative detailed description remains challenging due to their enormous compositional complexity. For this study, a typical light and sour Saudi Arabian petroleum crude oil was distilled into 27 narrow boiling range fractions, from a lightest cut boiling below 149 °C to a vacuum distillation residue with an atmospheric equivalent boiling point starting above 566 °C. Each fraction was then comprehensively characterized using a number of analytical techniques, including gas chromatography, comprehensive 2-dimensional gas chromatography, high performance liquid chromatography, and Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) in conjunction with photo- and electrospray ionization. Additionally, average cut properties were determined using nuclear magnetic resonance spectroscopy and standard methods, which included total nitrogen content (ASTM D4629), total sulfur content (ASTM4294), and specific gravity (ASTM D4052). The resulting data allowed us to expand on our previously reported application of FT-ICR MS for the (semi) quantitative speciation of sulfur components in gas oil samples [4] to cover aromatic compounds in petroleum heavy ends, including the vacuum residue fraction. This study established the performance envelope of each analytical technique with respect to sample boiling range, enabling the formulation of efficient strategies for the detailed characterization of intermediates and product fuels. Here, we show the molecular-level constituents of the studied crude oil and how the methodology was applied for a detailed sulfur speciation in visbreaker feed and product streams in support of meeting the International

Maritime Organization (IMO) 2020 bunker fuel sulfur specifications. To our knowledge, the novel aspect of this work is the first application of a full range of advanced analytical techniques to narrow distillation cuts that span the complete range of a petroleum crude oil. The attained near-molecular analysis method was applied to (semi) quantitatively speciate the high- and non-boiling sulfur aromatic compounds in a marine fuel and its refining feedstocks.

AROMATICS AND DIAROMATICS IN JET FUEL BY GAS CHROMATOGRAPHY VACUUM ULTRAVIOLET DETECTION - A NEW ASTM METHOD

Dan Wispinski, Jack Cochran, Alex Hodgson, Sean Jameson

Jet fuel specifications require the determination of aromatics. Early in 2018, a key component of the Fluorescent Indicator Dyed Gel needed to perform Test Method D1319 became unavailable. An alternative dye was substituted, but the reformulated dyed gel was later found to be unsuitable for the analysis of jet fuel, diesel fuel and gasoline samples. The manufacturer is working on a reformulated dye but it will not be available until well after 2019, if at all. ASTM Subcommittee J has been looking for alternative methods for the determination of aromatics in aviation fuels. Gas chromatography vacuum ultraviolet GC-VUV technology has shown great promise in the determination of saturates, monoaromatics, and diaromatic content by carbon number in aviation fuels. A new ASTM standard test method is being developed to provide a suitable alternative to D1319. The GC-VUV technique is currently used in the analysis of gasoline-range fuels (ASTM D8071). In the jet fuel range, saturates, mono-aromatics, and diaromatics all have distinct VUV absorbance spectra which allow them to be deconvolved from one another in a complex matrix. The GC-VUV method will analyze jet fuel in a 14-minute run and a 2-minute automated quantitation, reporting total saturates and aromatics comparable to D1319. In the same analysis, diaromatics (speciated by carbon number) are reported comparable to D1840. This paper will summarize the GC-VUV technique and compare to existing jet fuel analysis methods of ASTM D1319, ASTM D1840, ASTM D5186 and ASTM D6379.

SESSION 9 - SECTION 2: FUEL TESTING AND TEST METHODS

ASTM D8148 – BRING HAZE AND CLARITY RATING INTO THE MODERN AGE

Ranzy Morgan III

The Determination and Rating of automotive, aviation and turbine fuels and lubricants have traditionally been performed by highly subjective visual methods such as D4176 procedure 1 and 2 as well D6986 for jet fuel. ASTM D8148 introduces a Spectroscopic Technique for the measurement of a fuels Haziness or Clarity. This method offers easy operation and world-class spectroscopic analytical performance, this automated approach delivers the rapid, precise and reliable haze determination measurement capability needed for today’s demanding petroleum-

based process control and product quality assurance applications. These applications include all light/middle distillate fuels (gasoline, jet and diesel) and biofuels. These materials are produced and transported in significant quantities and in each case the absence of haze, or product clarity, is an important quality control / workmanship requirement. Consequently, the determination of haze content in a wide variety of petroleum and biomass based matrices is essential. After some background and an introductory overview of the D8148 apparatus, data is presented which demonstrates the power and flexibility made possible by this unique spectroscopic technology.

INVESTIGATION OF INNATE FUEL PROPERTIES BY EXCITATION-EMISSION MATRIX (EEM) FLUORESCENCE SPECTROSCOPY

Rachel D. Deese, Jeffrey A. Cramer, Thomas Loegel

Excitation-emission matrix (EEM) fluorescence spectroscopy is a non-destructive analytical technique that creates three-dimensional spectra produced by the fluorescence emission at varying excitation wavelengths. This method is well suited for characterizing complex hydrocarbon mixtures, such as diesel fuels, because of the unique fluorescence fingerprint of the conjugated hydrocarbons and aromatic moieties. As such, changes in these groups can be examined and monitored by EEM spectroscopy. The degradation of fuels during storage is a serious concern as fuel quality has a direct impact on the performance and service life of imperative equipment. This study measured the changes in the excitation-emission matrix of diesel fuels that had undergone the ASTM4625 stress test to determine if fuel stability could be predicted using EEM spectroscopy. Preliminary EEM spectroscopy results showed significant differences between stressed and unstressed diesel fuels and these differences varied based on whether the fuel was stable or unstable. The EEM spectroscopy data were further processed using partial least squares discriminant analysis (PLS-DA) which identified two EEM wavelength ranges that could be used to distinguish between stable and unstable diesel fuels: 1) 450-475 nm excitation/ 375-475 nm emission and 2) 425-465 nm excitation / 560-595 nm emission. Overall, EEM fluorescence spectroscopy has the potential to provide useful compositional information for predicting fuel quality and other fuel properties.

GCXGC HYDROCARBON METHOD ALIGNMENT ACROSS MULTIPLE DOD FACILITIES

Alison E. Metz, Thomas N. Loegel, Paul J. Wrzesinski, Gretchen R. Simms, Michael E. Peretich, Andy M. McDaniel, Richard A. Kamin, Daniel J. Baniszewski

The United State Department of Defense (DoD) uses multiple fuel types for military vehicle, ship, and aircraft propulsion. Detailed compositional analysis by GCxGC-FID has become an increasingly valuable tool in fuel analysis. Multiple labs have developed methods, but there has been no real effort to standardize the results. Given the increased DoD reliance on composition, a joint DoD team conducted an effort to standardize the testing among four separate laboratories. This effort involved studying the method details, data-analysis processes, reporting procedures, dataset variability, preliminary statistics, and accuracy of results. The objective of

this work is to create a collection of guidelines for GCxGC-FID that can be used to obtain accurate, reproducible hydrocarbon composition information to a level of detail that facilitates much more comprehensive root-cause fuel quality investigations and actionable knowledge.

EVALUATION OF AVIATION FUEL PROPERTY INFLUENCES ON DIESEL ENGINE PERFORMANCE

Terrence W. Dickerson, Andy M. McDaniel, Jim S. Cowart, Jeffrey C. Stabb, Diane E. Fricker, Richard A. Kamin

The United States Navy is continually looking to enhance operational capability. Currently, Navy vessels carry aviation turbine fuel (JP-5) for servicing aircraft and diesel fuel (F-76) for ship propulsion and electrical power. A study was conducted to evaluate the operational impacts of continuous use of JP-5 aviation fuel in ship propulsion and power systems. This paper will provide a global review of aviation fuel property effects on combustion and emission characteristics in diesel engines with a primary focus on the impact of lubricity characteristics, as determined from traditionally accepted laboratory-based lubricity metrics, on diesel engine fuel injection equipment wear. Multiple extended-hour full-scale diesel engine and fuel system rig tests, 500-1000 hours in duration, were performed using JP-5 and F-76. The relative sensitivity of a high-pressure common rail and a unit injector diesel engine fuel system was determined through comparative analysis of in-situ hardware measurements and pre and post-test component inspections. Additionally, a comparison between performance of used hardware, and conventional and new laboratory techniques for measuring wear is presented.

THE MEASUREMENT OF FUEL SULPHUR CONCENTRATION BY PORTABLE XRF SPECTROMETRY

David Atkinson

Current regulations, set out in Marpol Annex VI, prevent the use of marine fuel with a sulphur concentration above 3.5% in much of the World’s international waters (unless vessels are fitted with a scrubber). From 1 January 2020 this limit will be reduced to 0.5%. The same regulations will continue to ensure that only fuel with a sulphur concentration of less than 0.1% can be burnt in designated Emission Control Areas (ECAs), such as the Baltic Sea. The most cost-effective way of meeting the 0.5% sulphur limit will be to be blend the minimum amount of expensive, low sulphur, distillate with the maximum amount of cheap, high sulphur, residual fuel oil. These fuels will surf a very fine line between economics and legislative compliance. Going forwards, ships will need to be armed with the very best technology to ensure that they buy and burn compliant fuel in both the open ocean and in ECAs. Marpol Annex VI and ISO8217 already specify XRF spectroscopy for the purposes of measuring the concentration of sulphur in fuel samples. However, it is only in recent times that suitable instrumentation has become available for making measurements in the field. In this study a portable energy-dispersive XRF, which conforms to ISO 8754, was used to confirm that the many and various fuel deliveries made by a bunker barge met the agreed specification. All reported measurements

and any conclusions drawn from the study have been placed within the context of the relevant rules and regulations.

IMPROVED HYDROCARBON MIXTURES ANALYSIS BY SUPERSONIC MOLECULAR BEAM GC-MS WITH COLD EI

Aviv Amirav, Konstantin Tartakovsky, Moshe Rabaev, Regina Sinelnikov, Alexander B. Fialkov and Tal Alon

The Aviv Analytical 5977-SMB (Supersonic Molecular Beam) GC-MS with Cold EI (Electron Ionization) provides significantly enhanced molecular ions for all hydrocarbons and thus enables their vastly improved analysis including their isomer distributions. In addition, isomers and structurally related fragments mass spectral peaks are exhibited which enable their NIST library identification. Furthermore, extended range of compounds are amenable for analysis with short column and high column flow rates, including low volatility large oil and wax compounds that cannot be analyzed by standard GC-MS. In addition, the 5977-SMB GC-MS enables much shorter analysis time and improved sensitivity that could be up to and over three orders of magnitude better on the molecular ions of large hydrocarbons than what can be achieved with standard GC-MS. The isomeric content and its distribution affect all the major physical and chemical properties of oils and fuels, including: combustion efficiency, octane number, flash point, viscosity, lubrication properties, solubility and solvation power, boiling points and melting points. However, since current GC-MS cannot be properly used for isomer distribution analysis in view of weakness or absence of their molecular ions, this important subject is being ignored and represents an untapped opportunity. The presentation will demonstrate how the provision of enhanced molecular ions combined with extended range of compounds amenable for analysis and faster analysis dramatically improves GC-MS analysis of real petrochemical fluids and how it enables isomer distribution analysis for unique fuels and oils characterization.

SESSION 10: FUEL PROPERTIES AND EFFECTS

FLASH POINTS MEASUREMENTS AND PREDICTION OF BIOFUELS AND BIOFUEL BLENDS WITH AROMATIC FLUIDS

Jinxia Fu, Scott Q. Turn

The flash point of biofuels and petroleum fuels is an essential safety-related property for fuel processing, transportation and storage. Hydroprocessed renewable diesel (HRD-76) and synthesized isoparaffin (SIP), two biofuel blend stocks, were blended with commercial petroleum aromatic fluids (aromatic 100, 150 and 200) to investigate the impacts of aromatics on biofuel flash point and to formulate blends with identical flash point characteristics as NATO F- 76 marine diesel and JP-5 jet fuel. To overcome the complexity of the fuel systems,

COSMO-RS ("conductor like screening model for realistic solvation") was employed to predict the flash point of these biofuel + aromatic systems. COSMO-RS calculated the flash point of alkanes and aromatics present in biofuel and petroleum fuels and the flash point of SIP + aromatics binary mixture systems. Based on the pure compound and binary mixture predictions, COSMO-RS calculations were expanded to develop surrogate mixtures for biofuels and aromatic fluids. The surrogates were in turn utilized to predict the flash point of biofuel blends with aromatics and to formulate blends with the same flash point as petroleum fuels. The COSMO-RS calculation also assisted the selection of aromatics suitable for blending with different biofuels.

QUANTIFICATION OF ANTIOXIDANT DEGRADATION PRODUCTS AS INDICATOR FOR JET A-1 FUEL DEGRADATION BY GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC-MS/MS)

Marcella Frauscher, Nicole Dörr, Charlotte Besser, Alexandra Rögner

For the reduction of susceptibility to thermo-oxidative ageing of kerosene-type jet fuels, antioxidants, of which the specification only allows a limited spectrum of phenol-type substances, are added. One of these compounds is butylated hydroxytoluene (BHT), whose antioxidant effect is frequently described in literature. However, there is little information about the emerging degradation products, which can be formed during storage. Therefore, this study introduces a time- resolved artificial alteration and analytical method for the quantification of BHT and its degradation products in a model kerosene. The limitations of the determination of BHT in low levels with infrared spectroscopy are demonstrated. For unambiguous identification of the degradation products as well as quantification of the residual BHT amount and selected degradation products, in particular 3,5-di-tert-butyl-4-hydroxybenzaldehyde (HBA) and 2,6-di-tert-butyl-p-benzoquinone (BQ), GC-MS and GC-MS/MS were used. Limit of detection and quantification (LOD and LOQ) was determined for all three components below 1 ppb. The formation of BQ and HBA was observed shortly after the nascent degradation of BHT, while the oxidation rate drastically increased remarkably after complete consumption of both, the initial AO BHT and the monitored oxidation products BQ and HBA. Consequently, the amounts of antioxidant degradation products can be used as an indicator for the oxidation state of fuel, and can be measured in trace amounts with GC-MS/MS.

JETSCREEN PROGRAM: HIGHLIGHT THE IMPACT OF THE JET FUEL CHEMICAL COMPOSITION ON THE FUEL SYSTEM

Mickaël Sicard, Maira Alves Fortunato, Simon Blakey, Bruno Raepsaet, Frédéric Ser, Laurie Starck, Benjamin Veyrat, Axelle Baroni, Marie-Helene Klopffer

The study of the compatibility of a fuel with polymeric materials is an important topic in the overall qualification procedure of a fuel. Indeed, in a fuel system, many polymeric elements of very varied nature are in contact with the fuel that could affect the behavior and the durability of certain elastomeric compounds that are sensitive to fuel chemistry. The objective of that

study, done within the framework of the European program JETSCREEN, is to highlight the impact of the aromatic content on the behavior of the polymer materials. Three fuels were used: a Jet A-1 and two extreme fuels: high aromatic and zero-aromatic. The polymer materials tested are nitrile, fluorosilicone and fluorocarbon. Three tests were carried out. At ONERA, the work is conducted according to the soaking test procedure described in ASTM D4054. Mechanical properties of the gaskets and analysis of the collected liquid phases are carried out. At IFPEN, sorption/desorption tests are used to study the sorption process and to evaluate the cycling impact by measuring the mass weight gain/loss evolution and estimating the volume swelling for each polymer sample. As expected, the mass variation measured, is strongly dependent on the polymer-fluid couple (due to the interactions existing or not between the different types of molecules). At USFD, dynamic stress relaxation tests are carried out to understand interactions between the polymer and the fuel. The results showed that the nitrile is the material the most affected by the fuel composition. Important mass variations and loss of mechanical properties were observed.

JETSCREEN PROGRAM: IMPACT OF FUEL COMPOSITION ON AERONAUTIC EMISSIONS

D. Delhaye1, I.K. Ortega, A. Berthier, M. Sicard1 and C.Focsa

Aircraft industry global market forecasts (Airbus 2018, Boeing 2018) predicts an aviation growth of more than 4 % annually between 2018 and 2037. This trend is confirmed as well by the International Air Transport Association IATA (Lee et al. 2010). The aviation industry has identified fuel as one of their major tools to balance the increasing number of engines compared to the total emission impact. However, understanding the link between fuel composition and emissions is challenging. In the frame of JETSCREEN project, different combustion tests, ranging from laboratory to engine scale, are performed. In the present work we have used a Combustion Aerosol STandar (CAST) Generator especially designed to work with liquid fuel (Jing et al. 2003) and with a low fuel consumption. We have used this generator to study the emissions generated by up to 15 different fuels including: Jet A-1, Synthetic Paraffinic Kerosene (SPK), Alcohol to Jet (AtJ), AtJ/Jet A-1 or HEFA/Jet A-1 blends and different JetA-1 in terms of sulphur and/or aromatics content. We have measured the non-volatile and volatile particles number, mass and size distribution produced by these fuels at different flame richness (between 0.5-1.6).

SESSION 11: POSTER SESSION

INVESTIGATION INTO MICROBIOLOGICAL FUEL CONTAMINATION OF THE AIRBUS A380 DURING REFURBISHMENT, INCLUDING TESTING & APPLICATION OF KATHON FP 1.5 FUEL BIOCIDE

Oliver Rumford-Warr

During the initial stages of refurbishment for Airbus A380 aircraft, an internal procedure was developed to remove redundant fuel from aircraft wing tanks. A small volume of fuel/water mix continued to reside in the tank bottoms leading to early stages of Microbiological Fuel Contamination. Without physical access to the tank bottoms for retrieving contaminated fuel, a preventative regimen of biocide dosing with KATHONTM FP 1.5 was planned to combat the issue. Fuelcare worked with Airbus & Dow Microbial Control to develop the biocide regimen using KATHONTM FP 1.5 Fuel Biocide at the aviation recommended dosage of 100ppm. Testing was carried out at the Airbus FAL (Final Assembly Line) in Hamburg utilising Fuelcare dosing systems adapted to the fuel farm systems. The results were subsequently analysed by Airbus, Dow & Hamburg Institut für Hygiene und Umwelt. The testing resulted in a successful ongoing treatment regimen planned preventing Microbiological Growth.

STABILIZING POTENTIAL LOW SULFUR BUNKER FUELS

Nestor Soriano

The International Maritime Organization (IMO) is mandating a more stringent sulfur regulation on bunker fuel capping it at 0.5% from 3.5% sulfur by January 1, 2020 globally. This mandate is driven by IMO's response to increasing environmental concern in the contribution of the marine transportation sector to harmful emissions. The new Low Sulfur Fuel Oil (LSFO) is expected to result in over 80% reduction in sulfur emissions contributed by the marine sector. While blending resids with blend stocks not conventionally used for bunker fuel applications seems to be a straightforward solution, these new lower sulfur blends could potentially result in fuels with stability issues caused primarily by asphaltene precipitation. This may impact not only the handling and storage of these fuels, but more importantly may result to more serious operational problems such as filter blockage, damage to pistons, rings, and liners as well as combustion issues among others. In this study, binary and tertiary mixtures of possible stock blends suitable for the LSFO application are prepared and evaluated for compatibility and stability. The efficacy of certain polymeric chemistry in minimizing asphaltene precipitation in these blends will be demonstrated and discussed. The mechanism of action by which polymeric additives disperse asphaltenes in these blends will be presented. These polymeric asphaltene dispersants will allow refiners to utilize existing and more economical blend stocks, without the need for significant process modifications while meeting the more stringent sulfur mandate on bunker fuels.

DEVELOPMENT OF METHODS TO QUALITATIVELY IDENTIFY LUBRICANTS AND OTHER NON-POLAR FUEL CONTAMINANTS

Iwona A. Leska, Thomas N. Loegel, Jeffrey A. Cramer, Mark H. Hammond

Nonpolar substances such as lubricants, greases, and hydraulic fluids can contaminate mobility fuel supplies, potentially causing fuel stability and performance problems. A method to identify and quantify those high molecular mass compounds has been previously developed in our laboratory utilizing High-Pressure Liquid Chromatography with Evaporative Light Scattering Detection (HPLC-ELSD). Initial testing have shown that the method can be successfully used for detection of the target compounds. In this work we conducted comprehensive validation of the method using multiple contaminants in several fuel backgrounds and developed dedicated analysis software. Data for over seventy potential high molecular weight contaminants was collected in a diverse array of fuel backgrounds (JP-5, JP-8, F-76, ULSD, and HRJ) and used to construct pattern recognition algorithms to map chromatograms to contaminants, contaminant categories, and mixtures of contaminants. Then a standalone software application that can apply the validated modeling framework to externally-produced UHPLC-ELSD data was developed. The results show that data modeling strategies can be used to discriminate between different categories of contaminants, and even provide estimates of the amount of compounds. The ability to detect, quantify and identify these types of materials in fuels is a critical aspect of any failure investigation that is related to fuel quality. Developed method is a simple and robust for both the detection and identification of many possible fuel contaminants without the high operating costs associated with high-end mass spectrometry instrumentation.

IDENTIFICATION AND QUANTIFICATION OF POLAR SPECIES IN STRESSED AND UNSTRESSED DIESEL FUEL BY GCXGC-MS

Kristina M. Myers, Thomas N. Loegel, Matthew C. Esposito, and Robert E. Morris

The primary mechanisms through which fuels degrade in use often involve the formation of oxidized or polar species and one of the prevailing theories of the deposition of fuel insolubles is based on the higher polarity of these insolubles. Thus, the identification and quantification of polar species in fuel as it is aged or stressed, would be a valuable tool in understanding and characterizing the liquid phase chemistry. An analytical methodology to isolate and characterize the polar fuel constituents had been previously developed by the University of Dayton Research Institute for jet fuel. This method involves extraction of polar fuel constituents on a microextraction column, followed by GCxGC-MS analysis. However, while adequate for jet fuels, this method was found to be inapplicable to diesel fuels. In this study the jet polars method was modified and adapted to identify diesel fuel polar species in both stressed and unstressed fuel samples. This method also utilizes solid phase extraction, but the GCxGC-MS method was modified and optimized for diesel fuel, and appropriate standards were employed to develop a method that accurately identifies and quantifies the polar species in both stressed and unstressed diesel fuel samples.

INVESTIGATION ON PROPERTIES OF EX BLENDS AND ADVANTAGES FROM ADDITIVES ACTIONS DURING HANDLING AND LOGISTICS

Danilo Zufferli, Viviana Berto, Milena Mantarro

The United States and European Union have the mandate to increase the market share of biofuels to reduce GHG emissions. The EU adopted the Renewable Energy Directive (known as RED II) which includes a 10% target for the use of renewable energy in road transport fuels by 2020. Under 2007 Energy Independence and Security Act, the US set a target of 36 billion gallons of renewable fuels for road transportation by 2022. Bioethanol and biodiesel are currently the main biofuels available on the market in big quantities and bioethanol is the most widely used alternative fuel in the world. Advantages and disadvantages of the use of bioethanol as renewable fuels have been studied in order to identify its suitable and most proper use in blends with gasoline, together with its possible side effects. Properties of commercial gasoline blends, EX, can be modified by the introduction of bioethanol so an investigation on properties such as oxidation stability, corrosion behavior as well as the compatibility and the impact due to the solvent effect of bioethanol with all the components involved in storage logistics and engine must be considered. This paper reports the findings of a study performed on corrosive properties, oxidation stability and lubricity of different bioethanol-gasoline fuel blends, in order to evaluate possible side-effect on gasoline blends due to the addiction of bioethanol. The study also considers the action of additives in controlling the characteristics of gasoline- ethanol blends.

A TOOLKIT FOR THE CHARACTERISATION OF THE MICROBIOME IN TRADITIONAL AND SYNTHETIC FUELS

Myrsini Chronopoulou, Ruth Barnes, Joan Kelley, Alexander McFarlane

Fossil fuels have been a key commodity in routine daily activities and across the transport sectors. However, there is a constant demand for “greener” solutions, leading to increased use of alternative fuels, such as biodiesel. Our knowledge on microorganisms with the ability to utilise and grow on fuel components is mainly limited to those growing in fossil fuels. Thus, we are faced with a new challenge when it comes to the detection and prevention of microbial contamination in alternative fuels. Here, we propose a combined approach employing standard microbiology, analytical chemistry and molecular biology, to target the microbiome developing in alternative fuels and to allow comparisons with microbial communities known to affect traditional fuels. A series of microcosms containing an aqueous and a fuel phase (conventional and synthetic fuels to be tested) are established to simulate growth conditions in fuel systems. Microbial growth is assessed from both the aqueous phase and biofilms forming on a variety of surfaces. Gas Chromatography-Mass Spectrometry (GC-MS) is used to analyse the composition of target fuels and determine which fuel components are degraded by microbes over time. Next Generation Sequencing (NGS) followed by bioinformatics and comprehensive data analysis offers better insights into the drivers of the fuel microbiome structure. Ultimately, this knowledge can be leveraged to the development of new test kits for the timely detection of microbial contamination in novel fuel systems.

THE JETSCREEN MODEL-BASED JET FUEL SCREENING AND OPTIMIZATION PLATFORM

Bastian Rauch, Uwe Bauder, Simon Blakey, Chris Lewis, Patrick Le Clercq

The EU has set ambitious targets with at least 40 % of aircraft to be powered by low-carbon sustainable fuels by 2050 as part of broader emissions reduction efforts across the transport sector. The ability to evaluate, certify and deploy these new sustainable fuels is therefore critical to achieving that goal. Such fuels need to be derived from novel renewable non-fossil sources but must meet stringent aviation safety and performance requirements. To help establish a sustainable alternative jet fuel (SAJF) industry, the European H2020 project JETSCREEN is developing tools and methods to screen and assess alternative fuels using small- scale, low-cost experimental testing and advanced computer-modelling techniques. The goal is to reduce the substantial investment and time needed to achieve approval for a new alternative fuel under the ASTM D4054 international standardisation process by supporting a more intelligent and rationalised process within D4054. To give early stage fuel producers a rapid feedback on the potential performance of their product and to help streamline the fuel approval process a selection of distributed fuel sensitive models is combined into the JETSCREEN fuel screening and optimization platform. Initial activities were concluded and showed the feasibility and added value of using knowledge-based screening tools by successfully performing a model-based screening of a real alternative aviation fuel candidate in advance of the full ASTM D4054 process.

NOVEL SMALL SCALE ISOTHERMAL THERMAL STABILITY TEST

Seyed Yoosof Sadat , Simon G. Blakey, Ehsan Alborzi

The current Isothermal Temperature Thermal Reactor (ITTR) device at the university of Sheffield has the capability to provide chemical kinetic data to strengthen the understanding of fundamentals of liquid phase oxidation of hydrocarbons, Jet fuel in particular. Although the products of the autoxidation process are understood to some extent, further fundamental research is required to investigate the underlying reactions ultimately leading to the formation of carbonaceous deposits. The current ITTR rig consists of a fuel supply system, HPLC pump, tubular heater, water jacket followed by an on-line oxygen sensor with a tube length of around 3 meters long. This current formation has a number of limitations; it is a large device which requires a high volume of fuel (around 20L) and a greater power output, resulting in significant operational and maintenance costs. Also, there is a considerable region of non-isothermal flow at the entry and sampling small volumes of fuel for post-test analytical analysis is challenging. The rig has been re-designed with a much smaller formation in order to resolve these shortcomings. A 20-mL sample is run through pipes immersed into a dry block heater with sand-bath replacements which offers an evenly distributed temperature profile. Testing the fuel using a static system with no headspace enables us to have the desirable residence time, varying the time directly. Thermal analysis data shows that the non-isothermal entry region is avoided

and operational costs are minimised.

IDENTIFICATION OF JET FUEL CONTAMINATION IN JET ENGINE OIL OF FIGHTER AIRCRAFTS

Konstantin Tartakovsky, Regina Sinelnikov, Moshe Rabaev

Aircrafts, particularly fighter aircrafts, are designed with systems for optimal efficiency that utilize the aircraft's space and work synergistically. An example of such system is the cooling of jet engine oil MIL-PRF-23699, which is exposed to high temperatures and requires an effective and external-temperature-independent cooling system. Thus, oil heat exchangers are placed directly inside the aircraft’s fuel tanks and due to the fuel's high volume, the cooling process is very effective. In cases of cracking in the heat exchanger, the pressure created by the fuel on the external wall of the tank is higher than the internal pressure and as a result, the fuel contaminates the oil, which dilutes and compromises the oil’s properties. Early detection of crack formation inside the heat exchangers is critical for flight safety. If there is a lack of routine monitoring of fuel concentration, the problem can only be identified by observing an increase in the oil’s level. Currently, there are several standard methods for the detection of fuel contamination in oil at a concentration above 2%. Any dilution of oil by fuel harms the functionality of the oil, since it leads to an increased wear of the engine bearings as a result of a decrease in viscosity and lubrication of oil and the drastic decrease of the oil's flash point, which is a safety hazard. We developed a straightforward method for the detection of oil contamination by fuel with a 0.2% (w/w) detection of fuel in oil. At 0.2% contamination, properties of the oil such as flash point and viscosity are not affected significantly, so there is no risk to flight safety. The method, which makes use of a portable photoionization detector and a simple apparatus, can be utilized as a routine test in field laboratories. The semi- quantitative analysis it affords, allows one to make a go-no-go decision in field conditions. The method was tested and determined to be effective due to several cases in which cracking was detected in heat exchangers prior to the development of severe cracks and significant contamination of oil by fuel, thus preventing flight safety hazards.

KEY COMPLEXITIES ASSOCIATED WITH JET FUEL AND NUCLEATION OF WATER AND ICE IN AIRCRAFT FUEL SYSTEMS

Judith Ugbeh

The contamination and behaviour of water in aircraft fuel systems remains a significant area of global research interest following several aircraft incidents. Water and particulates in fuel may lead to ice formation. The resulting ice formed may eventually block the fuel filters and feed pipes creating safety problems. In order to engineer a lasting solution to the problem of ice in jet fuel it is important to identify precisely the conditions and features that may exacerbate this phenomenon. This work provides a detailed account of the recent advances and technologies in the literature indicating conditions that might lead to the nucleation of water and ice in aircraft fuel systems. The originality and uniqueness of this work is that there is no peer review paper

that focuses on the key complexities associated with jet fuel chemistry. The research contribution will help identify the significant knowledge gaps that exist in the literature highlighting routes to be investigated for future research.

SYNTHESIS OF DIESEL AND JET FUEL RANGE ALKANES FROM FURFURAL AND ACETONE

Zhiping Tao,Yan Rui

Catalysis synthesis of bio-fuel from biomass-derived platform chemicals has received tremendous attention. Here we report a high-yield synthetic route for the production of diesel and jet fuel range alkanes from biomass-derived furfural and acetone, through a tandem three-step process: (1) aldol condensation, (2) pre-hydrogenation and (3) hydrodeoxygenation. The overall yield of C11-C13 alkanes reaches 85.8% (98.2%×93.8%×93.2%) from furfural, which provides reference for large-scale production of bio-fuel from renewable biomass. C11-C13 alkanes, the synthesized diesel components, could also be used as jet fuel components when its freezing point decreases to -40℃ by isomerization.

BACTERIA ADAPTATION TO JET FUELS

Thusitha S. Gunasekera, Loryn L. Bowen, Lisa M. Brown, Osman Radwan, Oscar N. Ruiz

Bacteria have developed a wide range of specialized adaptive mechanisms to survive and proliferate in hydrocarbon rich jet fuel (Gunasekera et al., 2013; Environ Sci Technol. 47:13449- 58; Gunasekera et al., 2017; App Environ Microbiol; 83: issue 10 e03249-16). In an effort to understand their biology and genetic response to Jet fuel, we have sequenced genomes and characterized transcriptomes of number of Gram positive and Gram negative bacteria including Pseudomonas aeruginosa, Marinobacter hydrocarbonoclasticus, Nocardioides luteus and Gordonia sihwensis. We found bacteria use multiple metabolic and adaptive mechanisms to overcome fuel stress, among them preventing accumulation of toxic compounds in the cell, extruding toxic solvents and activation of DNA/protein repair mechanisms. Bacteria also produce biofilms in order to prevent from direct contact with hydrocarbons. In addition to the stress responses, bacteria have developed efficient hydrocarbon degradation mechanisms including strategies to emulsify hydrocarbons.

JET FUEL PROBLEMS AND SOLUTIONS: FROM REFINERY TO WINGTIP

Anthony Kitson-Smith, Alisdair Q Clark and Moshe Rabaev

The field of jet fuel properties and characteristics is of tremendous importance. While some comprehensive publications are available (e.g. "Aviation Fuels" By: Maxwell Smith, "Aviation Fuel Properties Handbook" By: CRC, ASTM D1655, JIG publications, GamGrams educational publication), the primary focus of the vast majority of the publications are the properties and

quality of jet fuel and comparison of different kinds of jet fuels and systems adhering to different civilian or military standards. As a contrast to the available publications, we propose an educational textbook that will encompass jet fuel problems and solutions. The book, written through international cooperation, will serve as a manual and will include a set of standards, aiming to extend the knowledge of jet fuel through examples of malfunctions, instructions for corrective maintenance, and suggestions for preventative maintenance. Topics that are intended to be covered in the book include the effects of the source of the petroleum on the quality of the fuel; issues that can arise during storage and transportation, pumping and filtration; typical challenges in military applications; laboratory methods for additives; contamination and compatibility research; aerospace fuel systems failure analysis; and many other issues that fuel engineers face using "well-to-wheel" approach.

Objective: The objective of this project is to provide a textbook that presents in a systematic and structured way the accumulated knowledge and experience in Jet Fuel Problems and Solutions.

Approach: Informal conversations were made with experts in the field of aircraft fuels. All the contacted experts (about 20), expressed their wish to take part in this project. Each expert will assemble a work team and will then write a chapter. The book will include 20 chapters, each containing 20-30 pages. The preliminary chapters' topics will include:

1) The Impact of Crude Sources and Processing on Jet Fuel Properties and Performances
2) The Properties and Performance of Jet Fuel from Alternative Sources
3) Additives in Aviation Fuels
4) Risk Assessment in Supply Chain and Logistic
5) Filtration Systems
6) Temporary and Permanent Storage Facilities
7) Fuel Stability
8) Common Practice in Aviation Fuel Handling Equipment
9) The Art of Representative Sampling
10) Monitoring, Prevention, and Treatment of Microbiological Growth
11) Corrosivity and Corrosion
12) Advanced Research Test Methods for Dissolved and Heterogenous Contaminants in Aviation Fuels
13) Army Applications
14) Navy Applications
15) Air Force Applications
16) Aerospace Fuel Systems Failure Analysis
17) The Effects of the Fuel Composition on Non-metal Materials in Aircraft Systems
18) The Influence of Fuel Complexity on Propulsion Processes
19) Aviation Gasoline
20) Switching between Fuel Types in Refueling Aircraft

EXPERIMENTAL STUDY OF THE AUTOXIDATION OF n-DODECANE AND 1,2,4-TRIMETHYLBENZENE

Soraya Aminane, Mickaël Sicard, Frédéric Ser, Lorette Sicard

During its course in the fuel system, the fuel is subjected to thermal stress, which is manifested by the formation of solid deposits in the fuel system and injectors, causing clogging phenomena and a malfunction of these devices. The notion of thermal stability, which in some cases, is illustrated by the formation of solid deposits in jet fuel, is related to the chemical composition and the presence of oxygen naturally dissolved in fuel. However, the understanding of oxidative fuel degradation is based on little known autoxidation mechanisms. Experimentally, the investigation of the oxidation sensitivity of jet fuel is carried out using the PetroOXY device, thanks to model molecules of linear alkane and monoaromatic type, n- dodecane (n-C12) and 1,2,4-Trimethylbenzene (1,2,4-TMB), respectively. First, the model molecules are studied pure in order to highlight their behavior under thermo-oxidative stresses. Secondly, these molecules were mixed in proportion 80 % n-dodecane /20 % 1,2,4-TMB, in order to model a fuel surrogate. Beyond a color change (colorless to yellow), the results revealed that the induction period is significantly lower for the pure molecules whereas for the mixture, the induction time is doubled. Moreover, the appearance of a gel, probably a precursor of solid deposits is observed, showing clearly the interactions between the molecules. The mechanisms involved during this process were determined from several analytical characterization techniques (FTIR, GC, GC-MS) allowing us to identify the products of oxidation formed but also the quantification of them using chemical techniques (Peroxide Value, Total Acid Number, water content).

INVESTIGATING THE AUTOXIDATION ACCELERATING REACTIONS OF PEROXIDES AND PEROXYL RADICALS USING HIGH LEVEL QUANTUM CHEMISTRY CALCULATIONS

Matthew R. Dwyer, Simon G. Blakey, Ehsan Alborzi, Anthony J.H.M. Meijer

Increases in performance and operating temperatures of jet engines have led to the fuel being used as a coolant to remove this excess heat. As a consequence, the fuel becomes thermally stressed, and undergoes autoxidation through radical reaction pathways, causing the formation of insoluble gums. Novel fuels appearing on the market, means the importance of a fuel's chemistry on its thermal stability is becoming critical. This work presents a fundamental and chemically detailed approach to this problem. The autoxidation process occurs through radical reaction mechanisms. This presents a challenge, in particular when modelling them using quantum chemistry techniques. This is particularly true for the reactions of peroxide species which link the initial oxidation process to the deposition steps. The propensity to conserve overall electronic spin angular momentum during reactions, means that high level multi-reference methods are required to properly describe them. Multi-reference self-consistent field theory calculations with second-order Rayleigh-Schrödinger perturbation corrections applied (CASPT2) were carried out to investigate the self-reaction of peroxides and peroxyl radicals. These calculations demonstrate that the reactions are intrinsically multi-reference and involve open shell bi-radicals. These reactions follow non-concerted reaction pathways which are

energetically more favourable than the corresponding homolytic fission of peroxides and proceed towards the formation of oxidation product. From our calculations, the self-reaction of peroxyl radicals, also appears to lead to the formation highly reactive singlet oxygen as a product. Singlet oxygen will accelerate the autoxidation of fuel by reacting directly with the hydrocarbons, acting as the initiation step.

DETERMINATION OF ELECTROSTATIC DISCHARGE HAZARD IN AIRCRAFT REFUELING OPERATIONS BY EVALUATION OF PLASTIC TANK FILLING

Shimon Pisnoy, Moshe Netzer, Ofer Levi and Moshe Rabaev

Occurrence of electrostatic discharge during aircraft fuelling operations has long been recognized as a safety hazard. The need to minimise the possibility of these discharges has led to the development of different practices, mainly adding static dissipator additive to the non-conducting jet-fuel. Nowadays, the static dissipator additive (SDA) is a well-established requirement in all the leading jet-fuel specifications and is in widespread use in the commercial and military aviation. Despite of this, Israel's Air Force (IAF) has rarely used it over the course of its existence. Fortunately, there is no recorded event of an electrostatic discharge that caused safety issues in the hundreds of thousands of fuelling operations that were carried out. Yet, these statistics are not enough for safely concluding to continue not using the static dissipator additive. In order to deepen the understanding of the electrostatic behavior, field experiment was conducted. An insulated 660-gallon LLDPE cylindrical tank was top and bottom filled with different fuel conductivities while recording the electrostatic field outside of the tank. By doing so, this worst-case scenario of fueling operation enabled us to measure the highest electrostatic fields, to analyze the electrostatic behavior and relaxation of the fuel, and to evaluate the electrostatic risk of fueling via different systems. The method developed in this research is simplified and doesn't require complicated instruments while providing the operator all the information he need to decide the necessity of the static dissipator additive.

ASSESSMENT OF HEFA, ATJ, GTL-S8 & FARNESANE AS AN ALTERNATIVE JET FUEL BASED ON ITS WATER SHEDDING CHARACTERISTICS

Judith Ugbeh

Previous studies have shown that impurities like surfactants in fuel have impacted the coalescing performance hence; the aircraft maintenance team adopted an additional operational practice which is commonly known as water sumping. Normally after bulk fuel transfers, fuels are allowed to settle in tanks and sumping is carried out to reduce the free water level. The water settling tests can measure the presence of surfactants in jet fuels yet, there is no reliable data that focuses on the water settling rate of alternative jet fuels that comply with or are very similar to the Jet A-1 specification. Additionally, as a result of compositional differences in the conventional and alternative jet fuels, it is not known if water will shed out at different or similar rate. Therefore, there is need for reliable data and new data where this is believed to be lacking. This work was designed to evaluate the water settling rate of five different jet fuels

made to different national standards in comparison with the convention jet A-1 fuel. The result from this work will help identify precisely some of the ASTM certified alternative jet fuels that are potential candidates for an increased blending portion with the conventional jet A-1fuel.

A COMPARISON OF THERMAL AND FLOW MODULATED GCXGC WITH DUAL FID-MS FOR AVIATION FUELS

Richard C. Striebich, Linda M. Shafer, Zachary West, Steve Zabarnick

Hydrocarbon type analysis has become an important technique in the screening and evaluation of jet fuel quality and alternative fuel suitability. GCxGC is routinely used to characterize fuels for hydrocarbon type; it incorporates both quantitative FID and qualitative MS identification with flow modulation. The simultaneous FID-MS is convenient since compound class groups are more easily characterized on the MS channel and then immediately applied to the FID for quantification. Recently, thermal modulation with dual FID-TOFMS has been developed for column systems similar to the flow modulation system; results are being compared for the two different modulators for hydrocarbon type of petroleum and alternative fuels.

DIESEL FUEL FLASH POINT REDUCTION CAUSED BY TRANSPORT SWITCH LOADING AND SPLIT LOADING- A WARNING!!!

Howard Chesneau

Gasoline apparently is the main source of contamination in diesel fuel at the retailers. The contamination is most likely due to the switch loading – hauling gasoline prior to hauling diesel fuel or split loading where a single tanker has compartments carrying different types of fuel. As we know, diesel flashpoint is one of the important parameters for determination of its use. In FY2015, Georgia Department Agriculture (GDOA) issued 229 stop sales of diesel fuel to the retailers, which was more than the stop sales due to sediments or water. A designed experiment (DOE) was conducted in the Georgia Department of Agriculture State Fuel Laboratory at Tifton to determine factors that may significantly depress the flashpoint of diesel. The experiment was conducted by Karsen Wynn, an intern at the Fuel Laboratory. A simple three factorial design experiment was selected to investigate the effect of flashpoint on 1) diesels with different flashpoints, 2) diesels with different amount of gasoline contamination (from 0.25 % to 0.75 vt%), and 3) diesel contaminated with summer vs. winter grade gasoline. Additional field studies were conducted to verify actual events. This poster will show what was found and alert both suppliers and consumers of the potential issues. It will also establish possible links as to how ethanol may be entering the diesel fuel systems contributing to the increase of corrosion episodes attributed to ULSD.