17th INTERNATIONAL SYMPOSIUM ON
STABILITY, HANDLING AND USE OF LIQUID FUELS
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Abstract Summaries

Chevron Award of Excellence in Honor of John Bacha:

COMPARISON OF PROBABILISTIC PROPERTY MODELS FOR THE PREDICTION OF JET FUEL PROPERTIES

Clemens Hall, Bastian Rauch, Uwe Bauder, Manfred Aigner

Model-based property prediction is considered a key enabler in the screening and design of new jet fuel candidates. Combined with two-dimensional Gas Chromatography (GCxGC) for the compositional analytics, they allow the prediction of fuel properties critical for the assessment of fuel candidates already from small volumes (5ml). As safety relevant use case the assessment of new aviation fuel candidates makes the consideration of uncertainties due to unidentifiable isomers, measurement and model uncertainty necessary. Recent developments yield several probabilistic modelling approaches that can estimate uncertainties as part of the property prediction. In this work we present three of those approaches: Direct correlation (DC), Mean Quantitative Structure-Property Relationship Modelling (M-QSPR) and Quantitative Structure-Property Relationship Modelling (QSPR) with sampling. The approaches use Monte-Carlo Neural Networks (MCNN), a Machine Learning algorithm for the underling regression of the properties from the GCxGC measurements. We assess their predictive capabilities for the modelling of eight safety-relevant properties like the freezing point and the cetane number for conventional and synthetic jet fuels. The predictive capability assessment is based on metrics that quantify accuracy, reliability and precision of the models. Identifying strengths and limitations of the different approaches, we provide recommendations for the practical application of the different models and the use of model-based property prediction for the support of jet fuel assessments in general.

SESSION 1: SUSTAINABLE AVIATION FUELS IMPLEMENTATION

100 % DROP IN SAF FROM VARIOUS D7566 PATHWAYS: A FIT FOR PURPOSE PROPERTIES EVALUATION

David Evans, Tony Marasigan, Nathan Matheson, Paul M. Rawson

With the aviation industry looking at net zero carbon emissions by 2050, the use of Sustainable Aviation Fuels (SAF) is vital to success to meeting this challenge. Currently there are seven pathways approved in D7566 but rely on the being blended with fossil fuel based jet fuel. The current availability and scalability of production of SAF is varied, leaving options of combining multiple pathways to produce a 100 % SAF without the requirement of blending with fossil fuels. Using fuel produced via the catalytic hydrothermal conversion route as the base fuel due to the aromatic levels, blends using ATJ-SPK, FT-SPK, HEFA-SPK, and SIP-SPK at the maximum blend ratios were prepared. The fuels were tested against the D7566 requirements for a finished fuel as well as thermal conductivity, enhanced thermal stability, chemical and physical ignition delay properties.

THE ROLE OF SYNTHETIC FUELS IN A SUSTAINABLE ENERGY SYSTEM

Achim Schaadt, Rober Szolak

The manufactures of internal combustion engines and gas turbines face currently a lot of challenges. Among these are the required drastic emission reductions of carbon dioxide (CO2) as well as harmful local emissions the most prominent. Therefore, the state of the art of synthetic fuels based on hydrogen as an essential part of the energy system is discussed. The utilization of hydrogen and hydrogen-based fuels is a promising option to reduce greenhouse gas emissions of heavy-duty vehicles, ships and air crafts. Hydrogen can be further converted together with CO2 via Power to X (PtX) concepts into synthetic fuels such as methanol and Fisch-Tropsch products offering both CO2 reductions and reduction of pollutants. Methanol can be used both as a fuel and as feedstock for further upgrading to fuels like dimethyl ether (DME), oxymethylene ether (OME), methanol-to-gasoline (MtG) and methanol-to-jet fuel. Methanol based jet fuel synthesis opens new opportunities in the sustainable aviation fuel (SAF) production field regarding process efficiencies, production costs and sustainability. It has been shown in process simulations that the target jet fuel product selectivity and the H2 efficiency (e.g. amount of hydrogen needed per liter or kg of the end product) are the main advantages of this value chain relative to other SAF production pathways e.g. Fischer Tropsch processes (FT).

SESSION 2: PROCESSING TECHNOLOGY DEVELOPMENT FOR SUSTAINABLE AVIATION FUELS

A NEW MANUFACTURING PROCESS FOR THE PRODUCTION OF SUSTAINABLE AVIATION FUEL FROM RENEWABLE FEEDSTOCKS

Dan Kadlecek

Sustainable Aviation Fuels (SAF) are establishing themselves as a viable segment within the aviation fuel industry. Many aviation stakeholders have committed to long term reduction targets regarding greenhouse gas emissions, and this places significant pressure on the industry to develop technologies to meet the growing SAF demand. SAFs produced from primarily biological feedstocks are commercially available today and production capacity is anticipated to grow substantially over the coming decades. However, the socio-environmental expectations set forth by international bodies such as ICAO, as well as the corporate aspirations of fuel suppliers, OEMs and airlines means that the necessary volumes of sustainable, biologically-derived SAF feedstocks may be limited. One possible solution to the potential limitations of biologically-sourced SAFs is the development of eFuels, which are derived from carbon dioxide and hydrogen produced from renewable sources. Fischer-Tropsch technology is today the only pathway that provides access to eFuels for the aviation space. In this paper, a new eFuel pathway will be discussed that provides optionality in the production of SAF from advantaged feedstocks.

CO-HYDROPROCESSING – A ROUTE TO SUSTAINABLE AVIATION FUEL

Alisdair Clark

Aviation represents a unique and critical part of the global transportation system, carrying 1.8 billion passengers in 2020 to link the countries of the world across oceans and continents. The Industry is built upon scientific understanding, with attention to detail for aircraft/engine design and fuel selection to deliver high levels of reliability, efficiency and performance. With environmental focus now on transport CO2 emissions, the Industry have sought to apply these principles to meet a new challenge, to achieve

- Carbon neutral growth from 2021
- Net zero CO2 emissions by 2050

Numerous options are being progressed to meet these goals, including engine/aircraft design, flight profile optimisation, carbon management and fuel technology. The focus of the present paper is on fuel technology, where the Industry have approved a number of aviation kerosenes derived from alternative sources to mitigate CO2 emissions. Technology options include stand-alone manufacture or utilization of existing refinery units for co-processing. Studies suggest the latter may reduce capital expenditure requirement by $0.33/gallon[6], a significant benefit to meet targets of 2% and 5% sustainable aviation fuel (SAF) production by 2025 and 2030 respectively. Currently co-processing of sustainable feedstocks is limited to 5% v/v in mixture with crude oil derived distillates. In this paper, the impact on aviation turbine fuel quality is examined through pilot plant studies where this limit has been increased to 30% v/v for bio-oils and Fisher Tropsch wax, both independently and in mixture.

CO-PROCESSING OF HYDROPROCESSED VEGETABLE OIL

Paul P. Wells, Daniel E. Kadlecek

Refinery co-processing of hydroprocessed vegetable oil (HVO) can provide an effective means of increasing the bio-derived synthetic aviation fuel (SAF) content of jet fuel with minimal capital investment. Co-processing of bio-derived material is currently limited to 5 vol% of either triglycerides, free fatty acids, and fatty acid esters or Fischer-Tropsch liquids. Both feedstocks require hydroprocessing and fractionation at the refinery to produce a viable product. Spare hydroprocessing capacity at a refinery is rarely available and expansion of an existing hydroprocessing unit or installation or a new unit is quite costly. HVO, originally intended as a blending component for diesel fuel, is commercially available and (as the name implies) has been hydroprocessed to remove unwanted heteroatoms, primarily oxygen. The boiling range of HVO, dependent upon the feed source and degree of hydroprocessing, could exceed the 300°C endpoint of jet fuel and therefore fractionation may be required during refinery co-processing. This research will explore the impact of co-processing different types and amounts of HVO on key jet fuel properties as well as non-hydrocarbon composition.

SESSION 3: IMPROVED FUEL QUALITY CONTROL

NEW METHODS FOR ANALYSIS OF QUALITIES OF FUELS AND NOVEL FUEL COMPONENTS

Marcella Frauscher, Adam Agocs, Martin Miedler

Changes in regulations and a growing awareness of the limit of fossil resources will lead to a rapid growth in terms of alternative future fuels due to a rising demand. In order to accelerate this development and make it more efficient design tools including stability studies and analytical methods may be used. Determination of the influence of promising fuel components in various blend level or certain additives can be achieved by tailor-made stability tests. These can either simulate fuel circulation in use, storage experiments or stability assessment tests. In combination with tools such as high-resolution mass spectrometry precursors of beginning degradation can be detected. Evaluation thereof is assisted with data evaluation techniques to ensure fast processing and easy interpretation Hence, a determination of the stability performance depending on different blend components is possible. Moreover, ideal additive concentrations of stability additives can be elaborated. This approach can be applied to various fuels and fuel components, thus replacing and supporting the development of future fuels.

ADDITIVE TRAIL-BACK EFFECTS IN MULTI-PRODUCT PIPELINES HANDLING LARGE VOLUMES

John Bennett, Hajar M. Essa, Asim H. Saleh, Khalid E. Butairi

Conductivity improver additives are widely used in ultra-low sulfur diesel (ULSD). Where diesel is being transferred through pipelines also used for the movement of jet fuels, it is necessary that the additives are approved for such multi-product pipelines. The potential for trail-back of additives from the ULSD into the jet fuel is investigated during the approval process by undertaking pipeline trials. A batch of diesel containing the additive is dispatched through a pipeline, then followed by a jet fuel batch that is monitored for the presence of the additive. These trial batches are usually small in size and of short duration due to the operational needs of the pipeline. Following the introduction of ULSD into a network that had previously only transported higher sulfur diesel without additives, it was observed that conductivity in the interface between the ULSD and the jet was higher than either of the parent fuels. One possible explanation was greater than expected additive desorption following the prolonged exposure time of the pipeline to the ULSD during normal operation, where batches of diesel may take several days to pass through a pipeline compared to typical short duration trials. A bench study was undertaken to look at the effect of a pipeline’s ULSD exposure time on the conductivity of the following jet fuel batch. It was shown that increasing the exposure time would also increase the amount of additive that was present in the following jet fuel. It was also seen that the type of additive could have an effect, with some appearing to have a greater persistence than others. When the additive trail-back persists beyond the physical transition from diesel to jet fuel, then greater attention should be paid to this phenomenon, including during the selection of the additive.

RECENT DEVELOPMENTS AND VALIDATION OF A MORE ACCURATE TOOL FOR FUEL CLARITY BY D8148 SPECTROSCOPIC METHOD FOR HAZE IN FUELS

Ranzy Morgan

Providing fuel with the necessary cleanliness has been desirable since the earliest days of motorized transportation. Engine manufacturers expend significant effort to protect sensitive components of modern high pressure fuel systems from fuel contaminants. With an unprecedented number of new fuel types and feedstocks entering the worlds fuel supply, the industry is becoming increasingly concerned about fuel cleanliness and clarity. Over the decades, engine manufacturers, fuel producers and fuel distributors, worked within ASTM to establish specification limits for fuel haziness and clarity. Because of the variability and subjectivity found with the current visible methods such as D4176 and because ASTM specifications may be applied anywhere within the fuel distribution systems, fuel pipelines and transport companies have traditionally not supported these efforts. During the last five years, major pipelines have worked closely to support the optics-based technology found in D8148. ASTM D8148 Haze Clarity index is an instrumental objective technique which eliminates the subjectivity of the visual haze methods. D8148 measures and reports haze results in two formats 1) Instrumental Haze Rating (IHR) ranging from 1-6 which is calibrated to be equivalent to the D4176 Visual Haze rating, and 2) Haze Clarity Index (HCI) ranging from 50-100. HCI provides greater resolution and specificity of fuel cleanliness. With the large amount of data provided in the recent D8148 Interlaboratory Study, as well as CRC report 675, which compares D8148 to D4176 and actual amounts of water in fuel samples, it may be the time to seriously reconsider putting measurable limits around fuel cleanliness. This presentation will review the D8148 method, recent ILS results along with the data and conclusions presented in CRC report number 675.

GRAPHENE OXIDE-BASED MICROBIAL FUEL FILTER: FROM LABORATORY BREAKTHROUGH TO FIELD DEMONSTRATION

Oscar N. Ruiz

Biocontamination can damage fuel and fuel systems, thus, it is critical to develop methods to prevent biocontamination. Filtration is a very effective way to maintain fuel cleanliness. However, even the best aircraft fuel filters can only remove particles of about 1 µm in size. Most bacteria have a diameter
of less than 0.5 µm requiring a 0.22 µm filter for effective filtration. Such filter would present a strong barrier to fuel flow and would lead to large pressure drops. Previously, we demonstrated the development of a graphene oxide (GO) nanomaterial fuel filtration technology proving 99.97% microbial filtration efficiency in the laboratory without the need of small filter pore sizes for microbial filtration. Now we show further development, maturation and validation of this technology into field-demonstrated microbial fuel filters for gas station fuel dispensers (diesel fuel pumps) and electric power generators. We describe the engineering, laboratory validation, and field testing that when into creating a fuel filter capable of providing >90% microbial filtration efficiency at fuel flow rates of up to10 GPM for about 60,000 gallons of diesel fuel. The filter has a delta-P of ≤4 psi, which is well below the maximum allowed for current filters. The filter is of modular design allowing easy scale up for applications such as jet fuel. The field

demonstration showed the functionality and durability of the filter under real use conditions helping to mature and de-risk the technology one-step further into implementation.

ORGANIC SOLVENT NANOFILTRATION – A SUSTAINABLE SEPARATION METHOD TO ENHANCE FUEL QUALITY AND PERFORMANCE

Marie-Sophie Haverkamp, Jan L.W. den Boestert*

Due to the depletion of conventional oil resources and the growing demand for renewable fuels, including sustainable aviation fuels (SAFs), an increasingly diverse range of feedstocks and processes is being used, creating fuels whose detailed properties may vary significantly. Each processing route and feedstock can lead to specific contaminants during processing or in the final fuel product. These require removal, by complex separation or hydroprocessing technologies, or mitigation by blending and blanketing. Dissolved large-chain molecules such as gums but also asphaltenes and metal trace components cause quality, stability and fouling issues during production and/or application. The removal by conventional technologies is difficult and mostly not economical or sustainable. New separation tools such as Organic Solvent Nanofiltration (OSN) may provide the solution. The inherent OSN separation principle enables efficient separation of dissolved molecules in the molecular weight above 300Da from hydrocarbon-based mixtures. In addition, OSN can remove typical undesired trace components such as water and metals. In the last decade, OSN has proven its industrial applicability and robustness for treatment in large-scale (petro-) chemical and hydrocarbon processing operations. More specifically, successful demonstrations in fuel-related applications have provided evidence that OSN may contribute to ensuring and enhancing fuel product quality. The objective of the presentation will be to provide an overall understanding of OSN and the maturity of the technology; and also, to present open-literature examples of fuel-related OSN applications. The innovative and sustainable character of OSN and its potential within the changing liquid fuels business will be demonstrated.

DEVELOPMENT OF A MONITORING SYSTEM FOR DIRECT ANALYSIS OF MICROBIAL CONTAMINANTS IN FUEL

Dr. Jiri Snaidr, Dr. Claudia Beimfohr

A significant and yet often underestimated problem in the storage of fuels is contamination with microorganisms. The growth of mainly bacteria in the tanks leads to fuel losses and considerable quality degradation. When used in engines and power plants, these can sometimes have catastrophic consequences. For example, contaminated kerosene can cause damage or, in the worst case, engine failure due to clogged filters. Establishing an effective monitoring of microorganisms is very important. Standard investigations are essentially based on cultivation methods in which the bacteria are grown on artificial media and can thus be identified and quantified. However, this falls short as they can not analyze whole biocenoses. Therefore appropriate technologies should take a holistic approach. The VIT® gene probe technology is a powerful tool here. With its help, bacteria and entire populations can be identified, quantified and visualized directly in the sample. So-called gene probes, small pieces of genetic material specific to a bacterial species or group, are coupled with a dye and introduced directly into the completely preserved bacteria. Only in bacteria that have a corresponding target site, the gene probe and thus also the dye is bound and cannot be washed off: the bacteria specifically start to glow in the sample and can thus be analyzed. Using different fuel samples, we demonstrate how entire biocenoses in fuel can be analyzed using VIT technology. Based on this, we have built a innovative monitoring system that follows a holistic approach and effectively controls microbial contaminations in fuels.

SESSION 4: GROUND FUELS - GASOLINE, DIESEL, BIODIESEL AND GAS OIL

FAME – QUALITY, APPLICATION AND CHALLENGES

Katharina Friedrich, Dr. Richard Wicht, Dr. Ingo Horn

The Association Quality Management Biodiesel (AGQM) was founded 1999 specially to ensure the quality of biodiesel. And this is still a large part of the AGQM's remit today. To ensure the quality of biodiesel in Germany, a separate QM system was developed which applies to all biodiesel producing and trading members of AGQM. The most important quality-determining task within the QM system is the unannounced sampling. The results from our members, which account for approx. 75% of German production capacity, are published anonymously in an annual report and show that the quality of biodiesel can be guaranteed, also for parameters that are critical for the exhaust gas aftertreatment system, such as alkaline and alkaline earth metals, sulphur, and phosphorus. For some critical parameters, AGQM has specified stricter limits to ensure the quality. In the area of research and development AGQM actively cooperates with the mineral oil, automotive and additive industries in various research projects and working groups, primarily to be able to prove the suitability of FAME in modern and future vehicles and ships under the current demanding technical boundary conditions. The current AGQM approval lists for passenger cars, commercial vehicles, and inland navigation show that biodiesel in various blending quantities and in pure form can already be used to reduce greenhouse gas emissions significantly.

MONITORING BIODIESEL BLENDS IN HEATING APPLICATIONS – EFFECT OF EXPOSURE CONDITIONS

Thomas Butcher, PhD, Ryan Kerr, Marty Haverly, PhD

The heating oil industry in the U.S. is aggressively transitioning from petroleum distillates to the use of biodiesel, including the use of 100% biodiesel (B100). The storage environment into which this is occurring in the 5 million homes affected includes pre-existing degradation products and possibly water on the tank bottoms, and extensive use of copper fuel lines after the fuel leaves the tank. This paper focused on in-field and laboratory measurements to evaluate the condition of heating oils after extended periods of time with different exposure conditions. This study found that the presence of copper in heating systems should not lead to significant operational effects from the formation of acids or filterable insolubles for either No. 2 petroleum distillates or their biodiesel blends. Exposure to copper can, however, affect the measured oxidative reserve (EN 15751) and acid number (ASTM D664) of a given fuel oil sample. The magnitude of this impact depends on a number of factors: the surface to volume ratio of the exposure to copper, access of the copper-exposed fuel to oxygen, residence time of the fuel in contact with copper, and the overall time before the fuel is burned. Measured copper content of fuels has been shown to increase following even short exposure periods. Sampling of tanks in the field for quality monitoring must avoid sample collection from the tank bottom or after copper lines.

AN OPTIONEERING EXERCISE INTO THE POTENTIAL FOR USING ALTERNATIVE, MORE ENVIRONMENTALLY FAVOURABLE FUELS THAN CLASS A2 OR CLASS D GAS OIL

Carl Atkinson

The 2020 UK HM Government financial budget statement included an intent to review the eligibility of applications using ‘red diesel’, on the premise that reducing the number of applications would lead to environmental benefits either by consumers using less of a more expensive fuel or using an alternative, more environmentally acceptable fuel. Following the announcement, under which EDF Energy would not qualify for tax-exempt status, an optioneering exercise was conducted to assess the potential for using alternative fuels/fuel-additive combinations as an alternative to Class A2 or Class D gas oils. The review was comprehensive and captured all aspects that a change in fuel would incur, including the practicality of change, the environmental benefits both short and long term, fuel availability and resilience both short and long term, and potential future trends in fuel development.

EVALUATION OF COLD FLOW RESPONSE OF ULTRA LOW SULFUR DIESEL (ULSD) IN COMBINATION WITH RENEWABLE DIESEL AND BIODIESEL

Jason A. Lennon, Jessica N. Grabowski, Casey Bouissey

The use of ultra low sulfur diesel (USLD) in cold regions is greatly affected by the composition of the fuel. The most common test method used to ensure low temperature vehicle operability is ASTM D6371 - Standard Test Method for Cold Filter Plugging Point (CFPP) of Diesel and Heating Fuels. ASTM D975 (Standard Specification for Diesel Fuel Oils) provides guidance on air temperatures in different regions of the United States during winter months, which may be used to inform CFPP targets. Interest in the use of green fuels (common names for these materials are biodiesel, renewable diesel, and hydrotreated vegetable oil (HVO)) has gained interest in order to limit the increased carbon intensity associated with the combustion of petroleum derived fuels. To date, there has not been an extensive study on the CFPP responsiveness of ULSD in combination with varying levels of both biodiesel and HVO; and their response to cold flow improver (CFI) additives. A study was performed to measure the impact of combinations of ULSD, HVO, and FAME at varying levels on CFPP depression with and without the use of additives. After performing this study, we found that fuels inclusive of biodiesel had diminished CFPP responsiveness to cold flow improver than fuels blended solely with HVO. However, in either case, blends made into ULSD with either of these fuel streams were responsive to CFPP depression with the use of cold flow additives.

THE IMPACT OF CHANGES TO UK LEGISLATION AFFECTING THE ELIGIBILITY OF COMMERCIAL CONSUMER’S USE OF DUTY EXEMPT DIESEL FOR ESSENTIAL OR EMERGENCY PLANT SYSTEMS.

Carl Atkinson

In the UK, to indicate that a diesel fuel has not attracted the standard rate of fuel duty (tax), diesel includes a red dye/markers to denote that it is tax exempt and this fuel is available for use in a range of specific applications such as agriculture, non-public road going vehicles, construction etc. The tax-exempt list also includes all applications on power stations used for emergency power generation, emergency pumping systems and steam generating boilers. The 2020 UK HM Government financial budget statement included an intent to review the eligibility of applications using ‘red diesel’, on the premise that reducing the number of applications would lead to environmental benefits either by consumers using less of a more expensive fuel or using an alternative, more environmentally acceptable fuel. Later, details emerged indicating that the changes, which remove almost all eligibility for diesel fuelled power station plant systems, would take effect on 1st April 2022 and that in advance of this date any procurement of fuel not expected to be consumed before this date, must meet the non-exempt requirement. This presentation describes the impact of this legislative change and assesses the practicality of transition from red duty exempt to white duty paid diesel, the resilience of fuel supply these changes invoke and the overall impact from an environmental perspective.

THE VERSATILITY OF THE GC-VUV ANALYZER

Dan Wispinski, Sean Jameson

The application of gas chromatography vacuum ultraviolet (GC-VUV) spectroscopy has gained acceptance as an analytical technique in the modern petroleum laboratory. The adoption of GC-VUV has been due to the flexibility and versatility of standard methods, the recognition by regulatory bodies and the adaptability to complex R&D functionality. In this rapidly changing world of liquid fuels the GCVUV technique is strategically positioned to encompass a broad range of conventional, non-conventional and renewable fuels. The VUV Analyzer Platform provides an automated, fast and accurate approach to analyze products ranging from propane (C3) to triacontane (C30). The platform was developed to seamlessly switch between four standard analysis methods using the same hardware and software. Standard method ASTM D8071 provides a regulatory approved automated, fast, and accurate approach to alternative multiple gasoline methods for benzene, ethanol, olefins and aromatics. Standard method ASTM D8267 provides an ASTM D1655 and DefStan 91091 specification approved method for aromatics in jet fuel. Standard method ASTM D8368 analyzes biodiesel and aromatic content in diesel fuels. The latest method, prEN17734 analyzes EN228 petrol for saturates, aromatics, benzene, and oxygenates including ethers. This paper will describe the latest ASTM and CEN developments for these four methods and how they integrate into one automated system - the VUV Analyzer platform. In addition to the standardized methods, the determination of advanced chemical and physical properties of petroleum products by GCVUV will be introduced.

SESSION 5: FUEL TESTING AND TEST METHODS

APPLICATION OF GCXGC-VUV FOR THE ANALYSIS OF SYNTHETIC FUELS

Dr. Max Jennerwein, Dr. Klaus Tröster

Synthetic fuels represent a genuine challenge for instrumental analysis methods, independent from their source (e.g. FT or MtG conversion, etc.) or their purpose (e.g. Gasoline, Diesel Fuel, Jet Fuel, etc.). The scope of application of established methods is often not suitable to deal with strongly diverging compositions of Synfuels or regarding the limits of detection of certain target compounds, respectively. Numerous analytical questions cannot even be answered since adequate methods do not yet exist. Thus, in order to analyze such novel fuels and feedstocks and to guarantee their quality, the development of adequate analytical techniques is inevitable. In the past years and decades techniques like comprehensive two-dimensional GC, mostly in combination with mass spectrometry or FID, and vacuum-UV detection for one-dimensional GC found their why in lab routine for the separation of complex samples. Unfortunately, those techniques are often not sufficient to answer certain questions completely. Some of these questions can be answered by the application of a hyphenation of both techniques. Previous publications and presentations have shown the successful application and advantages of GCxGC-VUV. In the present study the opportunities of GCxGC-VUV analysis methods and data processing using different types of software were investigated and evaluated.

SYNTHETIC AVIATION JET FUELS, RELATIVE PERMITTIVITY & AIRCRAFT GAUGING SYSTEMS

Ian Mylrea, Paul Pilkington

Fuel gauging systems use permittivity to estimate the mass of fuel on board jet aircraft during flight. Gauge accuracy relies on the relationship between temperature, permittivity and density of the jet fuel being the same as the historic norm. For fuels derived from alternative sources this relationship can be different than for fuels derived from crude oil. Measuring permittivity is difficult, and as noted in the CRC report, there is need for a dedicated method to measure jet fuel. This paper describes some new fuels in terms of permittivity and describes a new test method published by the UK Energy Institute for measuring the property.

USING A FIELD PORTABLE LC FOR DETECTING CORROSION INHIBITOR/LUBRICITY IMPROVERS AND METAL DEACTIVATOR ADDITIVES

Thomas N. Loegel, Iwona Leska

This presentation will show ongoing efforts focused on the development of a new high-performance liquid chromatograph (HPLC) method utilizing an ultra violet-visible light absorbance photodiode array (UV-vis PDA) detector for the determination of concentration of monomeric and dimeric fatty acids used as corrosion inhibitor/lubricity improvers (CI/LI) in fuels and presence and concentration of metal deactivator additive (MDA). Dimers of fatty acids, especially of linoleic and oleic acid, are a class of compounds that are widely used in many practical applications including paints and coating and can be used to prevent corrosion and/or decrease wear between metal-to-metal contact surfaces. The use of HPLC with a UV-Vis detector for the analysis of fatty acids is very challenging due the lack available chromophores in their molecular structures which typically would require the use of very low UV wavelengths (<200 nm) which is not practical for portable systems. The goal of this effort is to see if any CI/LI additives can be detect in their native form and to explore different derivatization strategies to add chromophores for these compounds along with various chromatographic conditions. We have shown improvements to the MDA separation method through the use of a mobile phase modifier trifluoroacetic acid. This chromatographic additives also shows promise in the separation of CI/LI additives for both monomeric and dimoraic formulations. Additionally, results of esterification or amidification derivatization strategies are shown.

DETERMINATION OF HYDROPEROXIDES IN LIQUID FUELS: A SYSTEMATIC COMPARISON OF TITRATIONS AND ABSORPTION METHODS AND THEIR INNOVATIVE COUPLING TO HPLC

Ryma Benrabah, Zaki El Sayah, Pierre-Alexandre Glaude, Philippe Arnoux

Hydroperoxides are major products in the autoxidation of hydrocarbon fuels and play a central role in oxidation kinetics. Their presence affects the oxidation rate, even at low concentrations, and, in turn, the thermal stability of fuels. Standard techniques for the quantification of hydroperoxides in fuel involve the reduction of the ROOH hydroperoxides by I-, yielding iodine (I2), and can be quantified by titration. These ASTM methods are known to be poorly reproducible and have inadequate lower detection limits and limited dynamic ranges [1]. In this work, several analytical methods for the determination of hydroperoxides in surrogate hydrocarbon fuels have been systematically compared for a known concentration of ROOH: titrations of iodine with thiosulfate (ASTM D3703) and triphenylphosphine [2] solutions with colorimetric and potentiometric methods and quantification of iodine by UV-visible absorption. n-Decane was used as the fuel surrogate and tert-butyl hydroperoxide as the controlled ROOH content. Our systematic study shows that the ASTM method based on colorimetric titration using thiosulfate aqueous solution is the least accurate because of the non-miscibility of water and n-decade which makes the UV-visible spectroscopy method is ineffective, contrary to titration methods with TPP in n-decane. As expected, the potentiometric method is more reproducible and accurate and UV-Visible absorption allows to reach lower detection limits. We show that the combination of the potentiometric titration of iodine with TPP and UV-visible absorption allows determining ROOH concentrations with low detection limits and a large dynamic range. The advantages of both methods have been used to develop a new analytical method based on their coupling to HPLC.

USING HIGH MAGNIFICATION OPTICS AND SHAPE RECOGNITION CAPABILITIES OF DYNAMIC IMAGING TO ACHIEVE A MORE ACCURATE ANALYSIS OF FUELS

Colin Dalton, Tod Canty

High magnification optical imaging techniques for characterizing hard particles, water and soft organic particles in fuels is crucial for managing the operation of equipment and extending operational life cycles. Traditional particle counting methods are unable to characterize between particles, hard and soft and misrepresent water and bubbles as particles. They are unable to detect particles <4µm, which can have a significant impact on operational equipment. They are often limited to off line lab environments where a process sample is taken to a lab and timely control is difficult. These methods do not provide continual analysis of the fuels. High magnification imaging systems lend themselves well to the analysis of fuels as they clearly differentiate between hard and soft particles, water and droplets down to 1µm in size based on the high resolution images and shape information obtained. This reduces the likelihood of characterization errors and enhances reproducibility, repeatability and accuracy. The visual capability allows the user to input his or her knowledge of the process to work in making meaningful analyses decisions. Imaging filters can be applied to the analysis that can distinguish solids from water droplets thereby doubling the capability of the instrument over non-visual equipment which cannot make this distinction. This paper describes a high magnification dynamic imaging system used for measuring particle (Hard & Soft) concentration and size in addition to water concentration based on providing a true 2-dimensional size and shape analysis. The paper will also outline the critical steps in measuring, sampling and the analysis of fuel for both lab and in-line systems.

THE FAST PEROXIDE ANALYZER

Bas de Jonge, Larissa Ram, Lou Cheng

Peroxides are reactive compounds that may impact product quality, promote unwanted side effects such as autopolymerisation, and present safety hazards such as the risk of explosion. Traditional methods often make use of iodometric titration methods like ASTM D2340 and D5799. These methods are susceptible to oxygen interference, causing false positives, expose the analyst to hazardous substances, and are time consuming. Furthermore, most iodometric titrations have lower quantitation limits of 1 mg/kg active oxygen with high uncertainties at this level. Da Vinci Laboratory Solutions has developed an automated alternative to the current titration method based on a flow injection system: the Fast Peroxide Analyzer (FPA). The FPA is based on the chemistry used in iodometric titration. HPLC hardware is used to pump iodide and acetic acid reagents through a dedicated reaction module after a sample has been injected by an automated liquid sampler or sampling valve. Any peroxides present in the sample will react with iodide to form iodine, which is detected by a UV-Vis detector. The system addresses the common challenges associated with the traditional titration methods by eliminating oxygen interference and chemical exposure due to the closed system, while simultaneously lowering detection limits, improving reproducibility, and lowering analysis time. The system can analyze liquid streams like; styrene monomer, alfa-olefins, and knocking engine reference fuels; liquified hydrocarbon streams like 1,3-butadiene; and solid hydrocarbon streams like dicyclopentadiene.

GCXGC FOR HYDROCARBON TYPE ANALYSIS OF AVIATION FUELS AND COMPARISON OF DIFFERENT MODES OF OPERATION

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

Hydrocarbon type analysis using GCxGC has become a popular way to characterize jet fuel (and diesel fuel) to determine quantitative levels of n-paraffins, iso-paraffins, mono-, di- and tri-cylcloparaffins, alkylbenzenes, cycloaromatics, di- and tri-aromatics. Like few other techniques, this method can quickly and accurately determine the mass percentage of each of these hydrocarbon categories. As its development progresses, comparisons of results within the same laboratory (repeatability) and comparisons of results between other laboratories running exactly the same method with the same equipment (reproducibility) were conducted for a limited number of samples. Because there are so many different modes of operating GCxGC (reverse phase vs normal phase and flow modulation vs thermal modulation, primarily), comparisons of results were conducted between a laboratory operating with normal phase flow modulation and another laboratory operating with reverse phase thermal modulation. By examining these comparisons, we hope to get an indication of the accuracy and precision of this technique, when collaborators use exactly the same instrumentation and conditions, and when both instrument and conditions may differ in process or approach. While larger comparative studies with other collaborators and more fuels are in-process, the comparison described in this contribution focuses on GCxGC accuracy and precision between two labs running normal phase flow modulation GCxGC and then two labs running different modes of GCxGC.

CHEMICAL CHARACTERIZATION OF NITROGEN- AND OXYGEN-CONTAINING COMPOUNDS IN LIQUID FUELS BY USING ELECTROSPRAY IONIZATION COUPLED TO A LINEAR QUADRUPOLE ION TRAP/ORBITRAP MASS SPECTROMETER

Mark Romanczyk, Thomas Loegel

The ability to detect and chemically characterize heteroatom-containing compounds (HCCs) in liquid fuels is critical as these compounds adversely affect fuel storage and thermal stability. To address these needs, Electrospray Ionization (ESI) coupled to a linear quadrupole ion trap/orbitrap mass spectrometer was used to chemically characterize oxygen- and nitrogen-containing compounds (OCCs and NCCs, respectively) in aviation and diesel fuels and a marine gas oil. After methanol extraction of the liquid fuel, the methanol layer was directly injected into the ESI probe. The OCCs and NCCs were ionized via deprotonation and protonation, respectively, with little to no fragmentation. Kendrick Mass Defect (KMD) values were determined for the protonated and deprotonated ions, and the values were plotted against their respective nominal Kendrick masses to facilitate comprehensive characterization. For example, up to ten individual homologue ion series of ionized NCCs (*i.e.*, $C_nH_{(2n+4)}N$, $C_nH_{(2n+2)}N$, $C_nH_{(2n)}N$, etc.) were detected in the aviation fuels with an overall mass range of m/z 100 – 314. Several proposed chemical classifications of the NCCs include: alkylamines, pyrroles, pyridines, indolines, tetrahydroquinolines, indoles, quinolones, carbazoles and triphenylamines. Further, up to twelve distinct homologue ion series of OCCs (*i.e.*, $C_nH_{(2n-7)}O$, $C_nH_{(2n-9)}O$, $C_nH_{(2n-9)}O_2$) were detected in the aviation fuels with an overall mass range of m/z 89 – 283. Proposed classifications of the OCCs include: saturated carboxylic acids, phenols, benzoic acids, indenols, hydroxytetralins and naphthols. The Kendrick Mass Defect plots showed clear differences when the disparate fuel types were compared and among the same type of fuel (*i.e.*, aviation fuels). Unknown ions derived from an aviation fuel and ionized model compounds were subjected to collision-activated dissociation (CAD) to facilitate further structural analysis. Several of the CAD spectra of unknown compounds were nearly identical to the model compounds. The information collected from this method may aid in providing more thorough chemical characterization of fuels, which may be used to provide stronger links between fuel composition and the propensity of fuels to fail storage and thermal stability.

THE IMPACT OF NON-FERROUS CORROSION INHIBITORS ON REACTIVE SULFUR SPECIES AND THE DOCTOR TEST

Matthew Barnes, Brandon Vittur, Sankaran Murugesan

It is well known that the presence of hydrogen sulfide can result in failure of copper and silver corrosion tests, and can be detected by several methods, including the doctor test. Additionally, the presence of elemental sulfur is known to cause non-ferrous corrosion issues but is more difficult to detect and quantify. The presence of mercaptans alone will not typically cause tarnish to silver, but in combination with elemental sulfur, form polysulfide compounds that tarnish silver. Additives containing alkyl dithiothiadiazoles are commonly used to correct copper and silver corrosion problems. In certain circumstances, these same additives were being tested in field locations and reportedly correcting failures of the Doctor test. It was not immediately apparent what mechanism might be allowing a fuel to become Doctor negative following non-ferrous corrosion inhibitor treatment. This paper presents a detailed experimental study to understand the nature of the interactions between non-ferrous corrosion inhibitor additives and mercaptans. A comprehensive mechanism is proposed by which the corrosion inhibitor may be affecting the Doctor test results.

SESSION 6: MICROBIAL AND CONTAMINATION/MONITORING

GENOMIC PROFILES OF MICROBIAL POPULATIONS IN DIESEL FUEL MICROCOSMS

Frederick J. Passman, Michael Waud, Kate Kucharzyk, Jordan Schmidt

The relationship between microbial bioburdens detected in fuel and fuel-associated water, and evidence of biodeterioration is unclear. Systems with negligible, detected bioburdens show evidence of substantial biodeterioration. Conversely, systems assessed to harbor heavy bioburdens sometimes show no evidence of biodeterioration. One hypothesis is that the types of microbes present in a system is a critical factor in determining whether a contaminant population is likely to be biodeteriogenic. Genomic testing was performed on aqueous-phase samples of microcosms used in a CRC-sponsored study to evaluate principal factors contributing to mild steel corrosion in diesel fuel underground storage tanks. The results presented in this paper indicated that initially, taxonomic profiles are dynamic but that after three-months they remain stable for at least 18 months.

INVESTIGATING THE EFFECT OF THE CONCENTRATION OF SEAWATER ON THE ACTIVITY OF SULPHATE REDUCING BACTERIA

Gareth J. Williams, Graham C Hill

Microbial sulphide generation in seawater compensated fuel tanks of ships, other vessels and oil platforms and has been reported for over 40 years. Sulphate, is utilised as an electron acceptor by a range of sulphide generating microbes, and is in plentiful supply in seawater. Hence, tanks and systems prone to seawater ingress are vulnerable to consequent microbial sulphide generation and Microbiologically Influenced Corrosion (MIC). In some circumstances, it is feasible to utilise freshwater as compensate water instead of seawater. This could reduce the levels of nutrients available for microbial growth and also the amount of sulphate available as a terminal electron acceptor, so mitigating this detrimental microbial process. This paper describes a laboratory investigation of the influence of varying proportions of sea water and fresh water on microbial sulphide generation and corrosion in simulations of seawater compensated fuel tanks. A series of microcosms containing naval distillate fuel and water with various seawater:freshwater ratios were inoculated with a consortium of microorganisms, including Sulphate Reducing Bacteria (SRB), from field samples. The extent of microbial growth and physico-chemical parameters of the water phase were monitored. The study sought to determine the overall effectiveness of using freshwater in compensate tanks to mitigate MIC. It also sought to assess the amount of seawater ingress that might be tolerated without a corresponding significant increase in SRB activity. Under the study conditions, levels of microbial sulphide generation were found to remain low providing sea water made up less than 25% of the compensate water.

ESTABLISHING AN ELECTROCHEMICAL BIOSENSOR FOR RAPID DETECTION OF FILAMENTOUS FUNGI AND YEASTS IN FUEL-CONTAINING ENVIRONMENTS

Osman Radwan, Michael C. Brothers, Victoria Coyle, Steve S. Kim

Fuels are not commonly thought of as a microbial growth medium. However, certain microorganisms have evolved the capacity to use fuel hydrocarbons as carbon sources, enabling proliferation in fuel systems including fuel storage tanks. Early detection of biocontamination would enable more effective implementation of mitigation strategies to prevent fuel system biodeterioration. Therefore, we developed a comprehensive method to develop a novel, reagentless, real-time, microbial sensor platform that is also fuel resistant. Firstly, we identified an extracellular protein epitope conserved in fuel-degrading fungi. Secondly, we used the epitope to identify a suitable biorecognition element (BRE) through biopanning of a 7-mer phage displayed peptide library and demonstrated the BRE's affinity to fungi with a fluorescence assay. Thirdly, we incorporated the BRE into a novel, reagentless real-time electrochemical sensing platform leveraging a mixed self-assembled monolayer containing a peptide BRE, redox reporter, and fuel-resistant fluorocarbon blocking group. Finally, we incorporated the real-time electrochemical sensing platform into a microfluidic device to demonstrate sensing of Yarrowia lipolytica extracted fuel. We demonstrated the detection of Y. lipolytica using the biosensor down to 1E4 CFU in a bath cell. In the microfluidic cell mode, the biosensor was shown to function after been exposed to jet fuel. Therefore, this work describes a process to generate fuel-resistant biosensors for detection of microbial growth in fuel system that can be leveraged in other applications including for food and biomedical pathogen detection. The biosensor platform described effectively detects multiple groups of fuel-degrading fungi including both filamentous fungi and yeasts.

INVESTIGATION OF HYDROGEN SULPHIDE GENERATION IN AN NDERGROUND SALT CAVERN USED FOR BUTANE STORAGE

Gareth J. Williams, Edward W. English, Howard L. Chesneau, Graham C. Hill

This paper describes the application of molecular microbiological techniques and chemical analysis to investigate problems of sulphide generation in salt caverns used to store butane, and the use of these methods for monitoring on-going risk. Following several months storage in a newly created underground salt cavern, butane gas and brine was found to contain elevated levels of hydrogen sulphide. This led to concerns over personnel safety and potential detrimental impacts on the infrastructure and product. An investigation was initiated to establish whether there was a microbial involvement in the problems being experienced, the potential long-term implications, and potential remediation plans. Samples of brine were obtained from the affected cavern and from an unconnected cavern that had been in service since the 1950s. A sample of water from the same well that was used to create the affected cavern was also collected. Samples underwent qPCR analysis to determine the abundance of bacteria, archaea and specific groups of microorganisms capable of generating sulphide (Sulphate Reducing Bacteria, Sulphate Reducing Archaea and bacteria belonging to the genus Halanaerobium). This was followed by Next Generation Sequencing (NGS) to identify the bacteria and archaea species detected in the samples. Chemical analysis of the samples was performed to ascertain the chemical and environmental conditions of the various systems, the availability of nutrients and chemical compounds needed to facilitate microbial metabolic processes, and the presence of specific metabolites associated with hydrogen sulphide production by microorganisms.

SESSION 7: IMPACT OF IMO 2020 ON MARINE FUELS

A HOLISTIC APPROACH TO MANAGING BUNKER FUEL QUALITY

Joseph Stark, Paul Biggerstaff

On January 1st, 2020 the International Marine Organization (IMO), in accordance with MARPOL Annex VI, adopted a new regulation for the maximum concentration of sulfur in fuel oil used on board commercial ships trading outside Emission Control Areas (ECAs). The new rule, commonly referred to as “IMO 2020”, states the sulfur content in bunker fuel must not exceed 0.50% m/m unless the vessel is equipped with an exhaust gas cleaning system (EGCS). Compliance with IMO 2020 effectively created a new fuel for the marine market, which is called VLSFO (very low sulfur fuel oil) and defined as a bunker fuel containing ≤ 0.50% sulfur. Although the implementation of IMO 2020 has been viewed largely as a success by the industry, fuel quality issues associated with the new VLSFO fuels have been prevalent throughout the marine supply chain. Producers and blenders are incorporating a wide variety of component streams to make VLSFO blends in order to economically meet the regulation. The increased complexity of these blends has resulted in a wider variety, and increased frequency, of fuel quality issues. These quality issues not only include traditional asphaltene destabilization, but now include paraffin wax crystallization and precipitation, sludge formation from various degradation mechanisms and solids fouling from inorganic particulates, such as catalyst fines, that can contaminate blend streams from refinery cracking units. While current test methods, primarily those found in the ISO 8217 fuel standard, help to identify fuel quality issues, one may not be able to determine the true root cause of the concern due to the complexity and variable nature of the fuels. Additionally, existing stability test methods were created before the onset of IMO 2020 and the creation of VLSFO. Current stability test methods only provide a snapshot in time on the stability of these fuels, they do not provide insight into longer term stability or operability. This is important issue as the industry has learned that the quality of today’s marine fuels can change over time. However, by conducting a detailed evaluation of a bunker fuel’s characteristics, its composition, and the operational dynamics of the application in which it will be used, a more complete, holistic understanding of the fuel's nature and behavior can be of achieved. This greater insight allows for improved economic decision-making during fuel design and blending, more efficient bunker operability in the field and greater success in predicting and mitigating any fuel quality concerns.

CATALYST FINES REMOVAL FROM SLURRY OIL-A NOVEL APPROACH

Sai Reddy Pinappu, Sankaran Murugesan

A new limit on the sulfur content in the fuel oil used on board ships came into force on Jan 1st 2020 (3.5% m/m before to 0.5% m/m current limit). This new limit on Sulfur is expected to improve air quality, preserve environment & protect human health. This made producers to look for new low sulfur fuel oil components, one such stream is, fluid catalytic cracking (FCC) slurry oil. Slurry oil is attractive to be used for blending down Sulphur content of fuel oils but the concentration of catalyst fines in this stream could exceed 1500 ppm. Per ISO 8217 - specifications of marine fuels, the limit on catalyst fines Aluminum (Al) and Silica (Si) is set at Al+Si <60 ppm. Traditionally, mechanical separation techniques such centrifugation & filtration are used to get the Al, Si concentration under specification but due to the nature of this hydrocarbon , catalyst fines are often coated with organic molecules which hinders the separation of Al & Si. In this paper, the effect of various physiochemical properties of slurry oil & effect of chemical additives on removal of Al, Si from the slurry oils will be presented. A Principal Component Analysis (PCA) was used to identify the important parameters effecting the separation.

INVESTIGATION OF WATER DISTRIBUTION AND MICROBIOLOGICAL GROWTH IN MARINE FUEL OIL BLENDED WITH FATTY ACID METHYL ESTER

Leon O'Malley, Graham C. Hill, Gareth J. Williams and Simon Ashton

Blending Fatty Acid Methyl Esters (FAME) with conventional automotive diesel fuel is known to increase the susceptibility to microbiological growth, with the potential for operational and quality issues. FAME is increasingly used in marine distillate fuels, with the 2017 edition of ISO 8217 including three grades allowing FAME up to 7.0 % v/v. More recently, blending FAME in heavier residual marine fuel oils has been trialled. In distillate fuels, microbial growth occurs predominantly in settled water phase. However, for fuels oils, the higher viscosity will result in a tendency for water to remain in suspension and consequently it is postulated that FAME may exacerbate active microbial growth within the bulk fuel oil phase. Using laboratory microcosms, this study investigated microbiological growth in Very Low Sulphur Fuel Oil (VLSFO) and VLSFO blended with FAME at 20% and 50% (v/v) at various fuel:water ratios. Although water settling was observed at higher water ratios, water distribution characteristics in all fuels were similar at fuel:water ratios reflecting those most realistic of field scenario. Where water did settle, high numbers of viable bacteria were detected in this, for all fuel types. Although the fuel oils were found to retain significant amounts of water in suspension, only limited microbiological contamination was detected in fuel phase for neat VLSFO and VLSFO/FAME blends. The results of this study suggest that providing marine vessel operators follow good housekeeping practices to minimize water accumulation, blending FAME in fuel oil should not substantially increase susceptibility to microbiological contamination in the fuel.

SESSION 8: FUEL CHEMISTRY RESEARCH
Part I: FUEL PROPERTY PREDICTION AND MEASUREMENT

REINFORCEMENT LEARNING FOR THE IDENTIFICATION OF ISOMERS WITH A STRONG SOOTING TENDENCY

Florian Pütz, Clemens Hall, Bastian Rauch, Andreas Huber

Predicting jet fuel properties based on the fuel composition is an important requirement for developing sustainable aviation fuels. The fuel composition at the molecular level can be determined by gas chromatography (GCxGC). However, the GCxGC cannot resolve most of the isomers present in a fuel. The missing information about isomers can results in significant uncertainties in predicted fuel properties relevant for determining combustor performance and emissions. For example, when estimating the yield sooting index (YSI) for an iso-alkane with 12 carbon atoms uncertainties of up to 30 % can be observed, depending on the branching degree of the isomers. For molecules with a short chain length the different isomers can be easily determined, but with increasing C-number, the number of possible structures grows exponentially. In this work, reinforcement learning (RL) is used to systematically explore the molecular space so that the molecule with the largest and the molecule with the smallest impact on properties like YSI, heat of combustion, viscosity, density or freezing point, will be identified. RL has the strength to independently find a strategy to optimize a reward function using a trial-and-error approach. The reward function can therefore be designed to maximize or minimize a fuel property. It is also investigated how the RL agent builds up the molecules or which structures have particularly large effects on certain properties. This min-max estimation, combined with the knowledge how a molecular structure should look like to optimize a particular fuel property, can help fuel manufacturers optimize their production process.

ANALYSIS OF TRACE COMPOUNDS IN MIDDLE DISTILLATE FUELS VIA SOLID PHASE EXTRACTION AND TWO-DIMENSIONAL GAS CHROMATOGRAPHY

Paul Wrzesinski, Linda Shafer, Richard Striebich, Zachary West

Analysis of middle distillate fuels, particularly jet and diesel fuel, has benefitted from developments in two-dimensional gas chromatography (GC×GC) for enhanced compositional analysis. While bulk hydrocarbon species analysis has been the primary focus for this technology, more recent, attention has been directed to better develop methods and techniques for determining the trace, heteroatomic components within these fuels. The work discussed here will highlight on-going efforts between DoD labs to develop a standardized approach for the execution of solid phase extraction (SPE) prior to analysis for trace components via GC×GC. The SPE approach both isolates the trace compounds from the bulk fuel matrix and provides a concentration enhancement. Emphasis will be placed on evaluation of different standards, developing an in-depth understanding of extraction efficiencies and observed differences between jet and diesel fuels. The discussion will also highlight the impacts of variations in analytical instrumentation and execution of SPE process.

IMPACT OF ISOMER SPECIFIC IDENTIFICATION ON FUEL PROPERTY PREDICTIONS

David Bell, John Feldhausen, Joshua Heyne

Petroleum fuels contain thousands of different unique hydrocarbon species. Describing the distribution of these species, frequently done with chromatographic methods, traditionally has culminated with hydrocarbon type analysis, sorting species based on carbon number and group type i.e., n-alkanes, iso-alkanes, aromatics, etc. This analysis can be applied to estimate the properties of the mixture. This level of detail with respect to hydrocarbon characterization has widely been accepted as sufficient. However, within each of these groups, there are hundreds to thousands of isomeric structures, which has a significant influence on the properties of the fuel and the capability of the fuel to perform. This research hopes to highlight the significance of variance in properties within a hydrocarbon group. The impact on properties of the specific species within a hydrocarbon group can be as significant as the hydrocarbon group depending on the property. These observations have led to the development of techniques using two-dimensional gas chromatography with a Vacuum Ultraviolet (VUV) detector. The VUV detector shows potential for isomer specific hydrocarbon identification. Results from this VUV detector demonstrate the improvement of property predictions with this information.

PROBABILISTIC SEQUENTIAL NEURAL NETWORKS FOR THE MODELLING OF JET FUEL COMPOUND PROPERTIES

Clemens Hall, Bastian Rauch, Uwe Bauder, Manfred Aigner

Jet fuels are complex mixtures of hundreds of possible molecular components. The modelling of jet fuels as mixtures requires the accurate and reliable prediction of physical properties of the molecular components contained in the fuel e.g. derived cetane number or net heat of combustion. The underlying algorithms need to correlate the molecular structure of the components with the desired property. Popular modelling methods like Group Contribution (GC) or Quantitative Structure-Property Relationship (QSPR) method only approximate the molecular structure by structural or physio-chemical descriptors. We present a method that directly correlates the molecular structure of components with the desired property. Using sequential Long short-term memory (LSTM) neural networks we predict properties on the line notation of the molecular structure, given by Simplified molecular-input line-entry system (SMILES). We make use of algorithms developed and used in the field of natural language processing for language translation tasks and transfer the concepts to the regression of molecular properties, considering not only the atoms of the molecules but also their order in the molecular structure. We model properties considered critical for the assessment of jet fuels of up to 1860 molecules and compare the predictive capability of the sequential models with the predictive capability of state-of-the-art QSPR models.

ANOMALY DETECTION VIA CHROMATOGRAPHY AND ONE-CLASS SUPPORT VECTOR MACHINES

Jeffrey A. Cramer, Robert E. Morris, Thomas N. Loege[1]

Failure and anomaly investigations are a regular occurrence in both routine fuel handling operations and non-routine fuels research. While underlying fuel problems can arise from gross contamination issues, subtle compositional differences can also lead to unwelcome synergistic interactions, especially during long-term fuel storage or during the course of downstream fuel commingling. Although near-infrared (NIR) spectroscopy has shown itself to be capable of sensitive anomaly detection, the broadness and convolution of the technique's combination and overtone bands complicate precise ab initio diagnostics. More informative anomaly detection procedures might be obtained via recently developed analytical methods based on gas chromatography (GC). However, quickly and accurately assessing the large and compositionally rich data sets provided by GC-based fuel analysis methods remains an ongoing challenge, especially if automated anomaly detection and diagnosis is the goal. A case study will be presented wherein a slightly anomalous diesel fuel, which evaded detection via less robust GC-based data assessment strategies, was automatically detected and characterized by modeling two-dimensional GC with flame ionization detection (GCxGC-FID) data with one-class support vector machines (SVM). This outcome demonstrates the practical potential of combining compositionally detailed fuel data sets with machine learning algorithms.

SESSION 9 FUEL CHEMISTRY RESEARCH
PART II: THERMAL-OXIDATIVE STABILITY R&D

DENSITY FUNCTIONAL STUDY OF THE DEPOSITION AND ADSORPTION OF FUEL SPECIES ON STAINLESS STEEL

Charlie Adams, Ehsan Alborzi, Anthony JHM Meijer, Simon Blakey

It has been well-established that the first stage of fuel deposition processes involve the adsorption of fuel species to the walls. Hereby, Stainless steel is often used as a substrate for deposition, given its commonality in industrial processes. However, the fundamental steel-fuel interactions are poorly understood and were researched in more detail here. We started from the premise that oxidized fuel species (alcohols, ketones, carboxylic acids) and/or fuel sulfur species (thiols, sulfides, sulfur acids) are involved in the early stages of deposition, given that elemental analysis from our aviation fuel thermal stability test unit (AFSTU) indicates a high concentration of sulfur and oxygen at the wall. To test our hypothesis, we employed the plane-wave DFT Vienna Ab-Initio Simulation Package (VASP) to model the fundamental interactions between adsorbate and different wall models. We used the OptPBE functional to calculate adsorption energies on Fe2O3 and Cr2O3, which were selected as two representative stainless-steel surface oxides. It was found that all acidic species chemisorbed on the metal terminated oxides, specifically at the metal top-sites. Interestingly, the sulfur-containing acids appeared to be more reactive to metal-terminated Cr2O3, whereas carboxylic acids were more reactive to metal-terminated Fe2O3. Thus, sulfur-free fuels are likely to have a different deposition mechanism than conventional fuels. Additionally, it was found oxygen-terminated Fe2O3 surface was able to abstract a hydrogen from both thiols and acids, suggesting that this termination may play a role in the initiation stage of autoxidation.

COMPARISON OF SELECTIVITY/REACTIVITY OF ZEOLITE COATED MONOLITHS ON IMPROVEMENT OF AVIATION FUEL THERMAL STABILITY

Ehsan Alborzi, Abby Samson, Simon Blake, Mohamed Pourkashanian

Strong selective adsorption of a number of heteroatomic species, as well as partial removal of dissolved O2 was observed upon treatment of aAviationa Jet A-1 fuel sample treatment with zeolite 3.7Å (also known as chabazite). exhibited a strong selective adsorption of a number of heteroatomic species, as well as partial removal of dissolved O2 . This is due to the crystalline structure of zeolites with which exhibit a network of cavities and pores, which collectively offerings a preferential adsorption for the molecules smaller than the size of pore diameters. Another important criterion that determines the nature of adsorption of species by zeolites is the ratio of Si/Al. Experimental evidence supported by quantum chemistry calculations suggest that the interaction of dissolved O2 with chabazite is of a physisorption nature, as opposed to the underlying process of oxygenated and other polar species removal by chabazite which is dominantly chemisorption. Chabazite monoliths, coated with three different Si/Al ratios were used in a lab-scale packed bed reactor, to compare the effect of selectivity and reactivity of the sorbets on improvement of the thermal oxidative stability of the Jet A-1 fuel. Three types of chabazite coated monolith with different Si/Al ratio w ere used in a lab-scale packed bed reactor to compare the effect of selectivity and reactivity of the sorbents on the improvement of thermal oxidative of a Jet A-1 fuel sample. The effect of bed length on improvement of fuel thermal oxidative stability was also studied. The thermal stability assessment of the treated fuels was carried out using a "High Reynolds Number Thermal Stability (HiReTS)". assessments showed thatThe treated fuel samples showed displayed a significant improvement of in reduced surface deposition propensity. via assessment with a "High Reynolds Number Thermal Stability (HiReTS)" Furthermore, the effect of bed length on improvement of fuel thermal oxidative stability was studied. Quantification of post-treatment samples demonstrated a substantial adsorption of dissolved Fe molecules. Quantum chemistry calculations were carried out using the ORCA 5 program package to elucidate the nature of the interactions of polar species with the inner and outer surfaces of chabazite. The polar species used in the ab initio quantum chemistry model calculations include Fe naphtanate, aniline, di butyl di sulphide, Butylated hydroxytoluene (BHT), hexanol, hexanone and hexanoic acid.

HIGHLIGHTING THE "STRUCTURE-REACTIVITY" RELATIONSHIP FOR THE AUTOXIDATION REACTION OF HYDROCARBONS

Soraya Aminane, Mickaël Sicard, Lorette Sicard, Frédéric Ser

One concern of the aviation industry is the jet fuel thermal stability. When not guaranteed, it leads to the formation of insoluble deposits in the fuel system and injectors which causing clogging and failures. The aim of this study was to investigate the mechanisms and kinetics reaction for hydrocarbon molecules composing jet fuel. Considering the complexity of interactions and the contribution of minor species on deposit formation, five model hydrocarbons were selected (n-dodecane and its isomers blend, n-butylcyclohexane, 1,2,4-trimethylbenzene and 1-methylnaphthalene) and subjected individually to oxidation using the PetroOXY device, focusing on the beginning of autoxidation ($\Delta P/P_{max}$ = 2 to 10 %). An experimental protocol was developed for the first time to identify and quantify precisely the oxidation products formed in the gas and liquid phases, using analytical (micro-GC, GC-MS, FTIR, SEC, HPLC) and chemical (PV, TAN, water content) techniques. This diversity of techniques made it possible to monitor the consumption of reactants, namely oxygen, which is always higher than that of the parent hydrocarbons suggesting competitive reactions. Although the oxygen consumption is globally similar for the all alkanes, it is variable for the aromatics. This illustrates their reactivity confirmed by the induction periods (IP). The characterization results showed a link between the initial hydrocarbon's structure and the nature and number of carbon atoms in the oxidized products. In addition, the tests performed at different temperatures (140,150 and 160°C) enabled the calculation of the overall and hydroperoxide dissociation kinetics constants reaction. Arrhenius parameters values obtained were higher for alkanes (Ea>120 kJ.mol-1, A~10+12 s-1) than for aromatics (Ea<110 kJ.mol-1 and A<10+09 s-1), confirming the "structure-reactivity" relationship of hydrocarbons.

WHY DEPOSITS LOOK ABNORMAL

David Abdallah

The JFTOT specification defines abnormal deposits as a deposit with a color that is neither peacock nor like those of the Color Standard. A deposits appearance consists of a blend of physical and chemical characteristics of the deposit. We will look at both contribution in an attempt to better understand the visual rating mysteries of many abnormal deposits.

FUNDAMENTAL STUDY OF JET FUEL OXIDATIVE DEPOSIT FORMATION

Krege M Christison, Gregory B. Boursalian*

When analyzed by Quartz Crystal Microbalance (QCM) under oxidative conditions, there is no deposit formation in hydrocracked jet fuel component due to the severe hydrotreating used in its production, which generally eliminates reactive, polar, and heteroatom-containing molecules. Using a hydrocracked jet fuel component as a baseline, compounds from classes that have been identified as significantly involved in oxidative deposit formation were spiked into jet fuel component and the resultant mixture was analyzed by QCM.[1,2] Several analogues from each compound class were subjected to this analysis to determine structure/activity relationships in precursors to oxidative deposit formation. For the spiked hydrocracked jet fuel components that formed appreciable deposits in the QCM, the deposits were collected for further analysis. Pyrolysis GC/MS is a technique that allows for the analysis of these deposits through thermolytic cleavage of chemical bonds, which breaks the deposits down into their fundamental components. These data offer insights into the mechanism of deposit formation. The spiked fuels were also analyzed by comprehensive GCxGC and LC/MS before and after QCM to monitor the amount of the precursor compounds and to detect any soluble reaction products.

AN INTERACTIVE, INTERDISCIPLINARY AND COLLABORATIVE DIGITAL PLATFORM FOR THE ASSESSMENT AND OPTIMIZATION OF JET FUELS

Uwe Bauder, Clemens Hall, Florian Pütz, Benedict Enderle

Fuel-aircraft interaction is a complex and interdisciplinary problem, which becomes clearly visible for example in the scope of ASTM D4054 approval process. Optimization or even changes within such a complex system are difficult, since changes of the fuel composition to improve a fuel performance property might in contrary lead to decrease of other performance properties or even to safety critical properties. Also, the current specification limits have been empirically evolved and might have led to an over-determined or non-optimal set, limiting the potential of SAF. The poster will provide an overview about the SimFuel platform, a digital tool that was designed to help solving complex problems like the one above. SimFuel connects distributed models and combines them with datasets and knowledge to gain additional insight. The platform consists of four main components: databases (20’000 fuels, 5300 single components), models, a distributed model environment and the human-in-the-loop concept. With its web-based dashboards, the platform can support expert groups (human-in-the-loop) to collaboratively, interactively and systematically use the data, models and workflows of the platform in their decision process. Major use cases on assessing different machine learning models for fuel property prediction, and applying SimFuel for fuel prescreening and optimization are presented in detail.

NEW TOOLS FOR UNDERSTANDING FUEL AUTOXIDATION AND DEPOSITION

Steven Zabarnick, Zachary J. West, Paul J. Wrzesinski

Three new computational tools will be described which assist in developing a better understanding of fuel oxidation and deposition measurements. These tools are (1) a Windows dynamically-linked library (DLL) which simulates jet fuel autoxidation kinetics as a function of time and temperature which can be called from any host application, such as Excel, Matlab, or Python; (2) a Partial-Least Squares (PLS) method for using fuel composition and fuel deposition measurements to determine species classes most responsible for causing deposits; and (3) a non-linear data fitting method for determining Generalized Logistics Function (GLF) parameters for Quartz Crystal Microbalance (QCM) oxidation and deposition profiles. The autoxidation DLL brings the ability to predict fuel oxidation vs. time and temperature without the need for advanced chemical kinetic software. The PLS method enables determination of important fuel species classes from large fuel composition data sets. The GLF fitting method provides the ability to obtain functional form fits to QCM oxidation and deposition, and also to determine global oxidation and deposition rates from these profiles. While these tools were developed for jet fuels, their use is applicable to a wide variety of fuel types.

IMPACT OF CLAY TREATMENT ON THE THERMAL STABILITY CHARACTERISTICS OF AVIATION TURBINE FUELS

Zachary West, Richard Striebich, Samuel Tanner, Susan Mueller

The thermal stability characteristics of aviation turbine fuels remain a topic of intense interest. Fuels that fail thermal stability requirements after entering the fungible fuel distribution system can be especially problematic to deal with. Disposition strategies range in cost, expedience, and fuel handling assets available, e.g., diluting the batch via blending operations, returning the batch to a refinery, and dosing the fuel with additives are possible options. Another option that has been proposed for field remediation of poor thermal stability fuels is clay treatment. Clay treatment vessels are present at various fuel handling locations, and are typically used to remove surfactants from aviation turbine fuels prior to filter-coalescer treatment. Clay treatment is also known to remove polar organic compounds that have been implicated as strong, negative factors influencing thermal stability of aviation turbine fuels. Recent projects, funded by DLA-Energy, have focused on the effects of clay treatment with respect to the thermal stability of aviation turbine fuels. An emphasis is placed on understanding the resulting chemical compositions as well as the overall impact/efficiency of clay treatment as a remediation strategy. Clay treatment was found to be a plausible remediation strategy for some fuels, under specific conditions; however, numerous caveats and questions remain for field practitioners who wish to employ this strategy. This presentation will outline our research findings to-date and provide recommendations for future efforts.

SESSION 10: AVIATION FUEL AND AVGAS APPLICATIONS

AVIATION FUELS PROBLEMS AND SOLUTION- AIRCRAFT FAILURE ANALYSIS INDUCED BY THE FUEL OR FUEL SYSTEM

Albert Schmidt, Dr. Moshe Rabaev, Yalfal Sium, Haim Juda

NTSB's CAROL database contains information about aviation investigations since 1983. CAROL database hold 22,384 records of aviation safety occurrences from 2008 to 2020, from which 1265 are classified as fuel related. Fuel related occurrence aviation safety occurrences is defined as an occurrence in which “One or more powerplants experienced reduced or no power output due to fuel exhaustion, fuel starvation/mismanagement, fuel contamination/wrong fuel, or carburetor and/or induction icing”. In this chapter we review the fuel system major regulatory airworthiness requirements, survey dozens of real fuel related aviation safety accidents and incidents, analyze each safety occurrence, demonstrate a systemized analysis of complex scenarios involving fuel and fuel systems and describe investigation practices and techniques.

SESSION 11: POSTER SESSION

AN INTERACTIVE, INTERDISCIPLINARY AND COLLABORATIVE DIGITAL PLATFORM FOR THE ASSESSMENT AND OPTIMIZATION OF JET FUELS

Uwe Bauder, Clemens Hall, Florian Pütz, Benedict Enderle

Fuel-aircraft interaction is a complex and interdisciplinary problem, which becomes clearly visible for example in the scope of ASTM D4054 approval process. Optimization or even changes within such a complex system are difficult, since changes of the fuel composition to improve a fuel performance property might in contrary lead to decrease of other performance properties or even to safety critical properties. Also, the current specification limits have been empirically evolved and might have led to an over-determined or non-optimal set, limiting the potential of SAF. The poster will provide an overview about the SimFuel platform, a digital tool that was designed to help solving complex problems like the one above. SimFuel connects distributed models and combines them with datasets and knowledge to gain additional insight. The platform consists of four main components: databases (20’000 fuels, 5300 single components), models, a distributed model environment and the human-in-the-loop concept. With its web-based dashboards, the platform can support expert groups (human-in-the-loop) to collaboratively, interactively and systematically use the data, models and workflows of the platform in their decision process. Major use cases on assessing different machine learning models for fuel property prediction, and applying SimFuel for fuel prescreening and optimization are presented in detail.

THE USE OF ULSD AND RENEWABLE DIESEL BLENDS AS AN EMERGENCY FUEL FOR AVIATION

David Evans, Tony Marasigan, Nathan Matheson, Paul M. Rawson

Military helicopters can utilise diesel fuels such as F-76 as an emergency fuel albeit with maintenance penalties and altitude restrictions. The initial certification of F-76 as an emergency fuel occurred when the diesel fuel was typically straight run and high sulfur. Since then, the fuel industry has undergone significant changes from a refining perspective such as the degree of hydroprocessing to reduce the sulfur level, inclusion of FAME in commercial diesel and most recently, the introduction of renewable diesel. This body of work investigates the performance of ultralow sulfur diesel (ULSD) and renewable diesel blends as an emergency fuel for aviation use. Initial testing highlights the improved thermal stability characteristics of ULSD and their renewable diesel blends compared to low and high sulfur diesel as well as traditional jet fuels.

AFRL RESEARCH ACTIVITIES ON FUEL EFFECTS ON COMBUSTION PERFORMANCE AND EMISSIONS

Edwin Corporan, Scott Stouffer, Tyler Hendershott, Veronica Williams

Interest in higher concentrations of sustainable aviation fuels (SAF) in jet fuel blends to reduce carbon footprint and environmental impact of aviation activities has increased the need to understand the impacts of fuel chemical and physical properties on gas turbine combustor operability (e.g., ignition, lean blowout (LBO)) and emissions. SAF chemistries and physical properties may vary significantly relative to conventional fuels and thus, merit investigation to ensure adequate combustion performance and safety of flight. A summary of major findings of research activities at the Air Force Research Laboratory’s Fuels and Energy Branch on fuel impacts on combustion operability on a single-nozzle swirl-stabilized combustor (referee combustor) and a T63 engine, is presented. Many of these activities supported the recently completed National Jet Fuel Combustion Program (NJFCP). Fuels studied include: SAFs, jet fuel blends, surrogates and single component fuels, which encompass a wide range of fuel chemical and physical properties. In addition, results of a study investigating the correlation of subcritical fuel decomposition products with LBO performance, and preliminary results on the impact of high temperature fuel injection (up to 500°F) on combustion performance and emissions of the referee combustor are discussed.

FUEL QUALITY IMPACT ON VINTAGE AIRCRAFT

Paul Rawson, Nathan Matheson, Glenn Pinnuck, David Evans

Heritage aircraft often have propulsion and fuel systems that were designed to run on JP-4 fuel which has different performance specifications to those used by current military aircraft. Whilst they remain kerosene fractions the impact on contamination and thermal stability can have dramatic consequences for these old engine types. A Vampire aircraft operated by 100 SQN of the Royal Australian Air Force suffered an uncontained engine failure inflight in 2022. Examination of the engine and the fuel from the aircraft indicated fuel thermal instability was a possible contributor to the failure. Fuel delivered to the aircraft was of very high thermal stability as measure by JFTOT and QCM stability techniques whilst that recovered from the aircraft was of very poor stability characteristics. Analysis found High concentrations of plasticizer's and materials potentially extracted from the fuel system which may have caused significant deterioration of the fuels stability leading to disrupted fuel spray patterns and damage to the combustor cans and nozzle guide vanes.

PREDICTION OF WATER SOLUBILITY IN PETROLEUM AND SYNTHETIC JET FUELS WITH COSMO-RS

Jinxia Fu, Scott Q. Turn

Comprehensive GC×GC chromatography provides novel characterization of complex liquid fuels. Standard GC×GC methods have been developed and included in ASTM D4054 for certification of new aviation turbine fuels and fuel additives, generating copious compositional data. The present work utilizes the conductor-like screening model for realistic solvation (COSMO-RS) method to calculate water solubility in petroleum and sustainable aviation fuels (PAFs and SAFs) over a temperature range of -40 to 50 °C using GC×GC composition data. The calculation results are in good agreement with experimental values at temperatures below 20°C, with RMSE = 17.1 and 17.7 ppm for PAFs and SAFs, respectively. Results calculated for these complex fuel chemistries predicted experimental values more closely than calculations performed for simpler PAF and SAF surrogates. COSMO-RS was also employed to calculate water solubility in PAF and SAF blends (RMSE = 18.3 ppm). Results demonstrate that the COSMO-RS method has potential as a tool in new SAF certification.

STATIC DISSIPATIVE ADDITIVE PERFORMANCE AND STORAGE STABILITY IN BIODIESEL BLENDED DIESEL

Sankaran Murugesan, Asha Patel, Matthew Barnes, Don Wolfe

Static Dissipative Additives (SDA) are used to facilitate the safe dissipation of electrostatic charges through liquid hydrocarbon by reducing the accumulation of hazardous surface charges. Recently, there has been growing interest in the production and use of biofuels and renewable fuels as an alternative to conventional distillate fuels. It is expected that any transition from convention fuels to lower carbon intensity fuels will transition slowly in the marketplace. As such, there will be a period of time where the various fuels will be comingled. Addition of biofuels to distillate fuels can cause both synergistic and antagonistic effects. Industry has examined the impact of adding biofuels to conventional fuels for some common performance specifications such as lubricity. However, it would appear that such a study investigating the role of biodiesel on conductivity performance has not been explored. This presentation gives a comprehensive study of conductivity performance of biodiesel blended with Ultra Low Sulfur Diesel (ULSD) treated with SDA. Furthermore, this provides a detailed discussion on SDA dose variation with temperature and the synergistic effect caused by the presence of biodiesel.

DEVELOPMENT OF A SHIPBOARD TEST KIT FOR DISSOLVED COPPER IN JET FUEL PROTOTYPE FIELD TEST KIT

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

The U.S. Navy is currently investigating shipboard inline copper sequestration technologies to remediate the deleterious impact of dissolved copper on ship propulsion and aircraft engines. In the event that such technologies are deployed, a convenient means to monitor copper content would inform ship crews as to when to change out adsorbent media. A spectrophotometric procedure was previously developed at NRL to measure low PPB levels of copper in jet fuel, which utilized the underivitized form of bathocuproine (BCP), with ascorbic acid as a reducing agent. Since BCP only responds to Cu(I), this eliminates the need for post-analysis data treatment to resolve other interfering metals. In addition, uncomplexed BCP is colorless, eliminating the need to add BCP to the reference sample or remove copper from the reference fuel sample of interest. By utilizing standard additions of a copper standard, the BCP procedure will determine total copper content without the need for a copper-free reference, even in the presence of strong chelating agents, e.g., metal deactivating additives. Minor improvements to the previous method were made to improve the chemistry and extend of the method to measure copper contents of diesel and MGO fuels.

HANDLING, MAINTENANCE AND SAFETY USE OF AVIATION FUEL-INFORMATIVE BULLETINS

Maor Saban, Dr. Moshe Rabaev, Yalfal Siyum, Liel Mazar

Optimal care and maintenance of aviation fuels and infrastructure is of crucial importance for ensuring the safety of passengers, personal and the environment. In order to Increase the awareness of fuel technicians, engineers and decision makers in our organization for the safety issues regarding the maintenance and handling of fuel in the field, we have produced numerus Informative bulletins written in simple and convenient language, which makes it possible to convey important and essential knowledge in easy, digestible manner for every reader. Topics covered in the bulletins include information about "Apple Jelly" (see appendix 1), microbial contamination (see appendix 2), fuel filters, static electricity, aviation fuel additives, laboratory tests, critical fuel properties, fuel contaminations and real fuel related aircrafts safety events - emphasizing how a minor human mistake can have major safety implications. The bulletins have greatly raised the awareness of our organization personal while handling aviation fuel, and therefore we find it essential to share them with the wide global community.

INVESTIGATIONS INTO AUTOMATIC GENERATION OF A MECHANISM FOR AUTOXIDATION OF N-DECANE USING REACTION MECHANISM GENERATOR (RMG)

Seyed Yoosof Sadat, Dr. Ehsan Alborzi, Dr. Kevin Hughes

The detailed mechanisms explaining the autoxidation of jet fuel available in the public domain are normally constructed based on one single block surrogate fuel. With the introduction of alternative aviation fuels to the industry, an understanding of how different building blocks of hydrocarbons would behave in the system is crucial. Introducing extra blocks of surrogate fuel such as cycloparaffins to the model would add an extensive amount of computational work, which could be significantly expensive in terms of time, and the manual handling of it would be almost impossible. In order to avoid the expensive computational power required and add complexity to the detailed mechanism, an open-source computer code written in Python called the Reaction Mechanism Generator (RMG) was selected for auto-generation of a detailed mechanism. RMG uses a basic understanding of how chemical species behave on a molecular level to construct a detailed reaction mechanism and its kinetic parameters. The software has been widely used in the gaseous phase, however understanding of it remains limited in the liquid phase. In this study, RMG has been deployed to autogenerate a chemical kinetic mechanism for autoxidation of n-decane and it has been further merged with Decalin as a cyclo-paraffinic block. Following that a numerical technique has been used to reduce the mechanism by grouping and lumping method. The reduction method is able to overcome the complexity while the robustness of the mechanism is preserved to make it ready for further applications. Following the successful validation of the mechanism with experimental data, further hydrocarbon blocks could be integrated to it.

FOSSIL AND ALTERNATIVE FUEL DEPOSIT FORMATIONS UNDER REPRESENTATIVE OPERATING CONDITIONS

Mickaël Sicard, Bruno Raepsaet, Soraya Aminane, Yanis Melliti

In order to simulate the shutdown phase of an aircraft engine and the degradation of the fuel film in a hot environment (engine radiation), a specific test bench has been designed at ONERA to study the coking behavior of fossil and alternative jet fuels. Dynamic conditions, that is to say with a continuous flow of fuel, are followed by "stagnant" phases. A thin film of fuel remains inside the pipe and is maintained under air at around 200 °C. The relatively slow kinetics of deposits formation requires to accumulate a significant number of tests and thus stagnant phases. At the same time, it also helps to observe the cumulative effect of deposit growth. At the end of a long series of tests (30 flow and 30 stagnation phases for each fuel), the formation of solid deposits on the flat part of the diaphragm injector was observed. The aim of this study was to characterize and quantify the deposits formed by various techniques (DOM, SEM, EDS, FTIR, AFM…) to observe their growth by cumulative effect and their evolution with time. As expected, the most important quantity of deposits was obtained with the Jet A-1 but deposits were also observed for alternative fuels. The deposit starts with a few “islets” caught in a gel-like substance. During accumulations, these individual islets coalesce to form a continuous layer that reaches several microns thick. The quantitative evolution of deposit is an important challenge because it provides data mandatory to calibrate the models for numerical simulation.

EXPERIMENTAL STUDY OF THE IMPACT OF BIOALCOHOLS STRUCTURE ON THE OXIDATION STABILITY OF A SURROGATE JET-FUEL

Ryma Benrabah, Zaki El Sayah, Minh Duy Le, Pierre-Alexandre Glaude

The addition of biofuel in jet fuels can be seen as a promising answer to reduce the carbon footprint of the aviation transport sector. [1][2] In this work, we investigated the impact of the addition of alcohols on the oxidation stability of a jet fuel surrogate. Different chemical structures of bioalcohols were considered and were blended with n-decane which was used as the jet-fuel surrogate. The thermal oxidation stability of the mixtures was measured in a standard PetroOxy apparatus, which gives an induction period (IP). In addition to this global indicator of the fuel thermal stability, we quantified the total hydroperoxide concentration at the end of the test by iodometric titration. [3] The influence of the carbon chain's length in alcohols (n-butanol to n-decanol) and the isomeric structure of butanol on the IPs of pure n-decane have been quantified. We show that the addition of a low percentage by volume of bioalcohols in the fuel increases its oxidation stability. This effect is non-linear, and the IP value increases with the volume percentage of bioalcohol in the fuel up to 15%. Beyond this value, a rapid decrease in the stability of the mixture is observed. The influence of the carbon chain's length of the alcohols is shown to be negligible. In contrast, the structure of butanol isomers strongly impacts the stabilization efficiency of the alcohol in the fuel. Conclusions on the fundamental chemical mechanism are drawn from these experiments and highlight the central role of aldehyde formation in alcohol oxidation kinetics.

HYDROCARBON MULTIDIMENSIONAL GAS CHROMATOGRAPH TEMPLATE OPTIMIZATION STUDY

John Feldhausen, David Bell, Joshua Heyne

Multidimensional gas chromatography is one of the most popular analytical chemistry separation techniques and is valuable in characterizing the hydrocarbon composition of jet fuels. Important operability and safety properties can be predicted from the results of a chromatograph provided the stencil making the various hydrocarbon classifications was properly calibrated. For those interested in building a hydrocarbon template from the beginning, in such a way that it reproduces the exact results of calibrated template, can be challenging. Existing chromatography literature attempts to instruct template development, but inconsistencies between various instruments is still likely, and can be difficult to source and quantify. This work proposes a solution to the struggle of bridging various separate gas chromatography instruments with an optimization approach that receives an initial guess of group coordinates from one template and minimizes the difference in the results against a separate specified baseline template. In this way, a proven template can be leveraged to guide the construction other templates. With this technique, compositional results from separate groups will be much more reproducible and the differences between groups can be used to determine relative uncertainties.

PREDICTING THE INSOLUBLE FORMATION TENDENCIES OF FUEL HETEROATOMS AND AROMATICS WITH COMPUTATIONAL TECHNIQUES

Charlie Adams, Ehsan Alborzi, Kevin Hughes, Anthony JHM Meijer

In recent years, quantum chemistry (QC) methods have started to be used as a tool to build predictive thermal oxidative degradation models for jet fuels from 'first-principles'. Nevertheless, QC work has solely focused on the first stage of the degradation process involving substrate activation and autoxidation. The second stage, agglomeration, and subsequent insoluble formation has not yet been studied with QC techniques. The complexity of the agglomeration process, where C-C/C-O bonds are formed leading to successively larger macromolecules, has meant it has been difficult to isolate a specific set of reactions to predict deposition tendency. To overcome this complexity, we proposed a chain-growth free radical reaction forming a deposit dimer from an array of fuel aromatics and heteroatomics. Furthermore, it was assumed that the deposit consists of heteroatom monomer units, allowing moles of deposit to be calculated. The calculated energetic barriers for the chain-growth reaction were then compared with total insolubles and extraction induced precipitate (EIP). The two component fuels contained n-dodecane and the selected aromatic/heteroatom of interest. The fuels were stressed in a glass flask at 140 °C with 1 bar molecular oxygen headspace for a duration of 24 h. It was found that the largest calculated transition state barrier provided a reasonable correlation with the molar amounts of deposit generated. However, a much stronger correlation was found between the EIP moles and the rate determining step.

THE EFFECT OF SPACING FUEL BLEEDING REGIMES ON AIRCRAFT TANKS MICROBIAL CONTAMINATION LEVELS

Liel Mazar, Alexi Bikbulatov, Yalfal Sium, Dr. Moshe Rabaev, Haim Yehuda

Microbial contamination in aircraft fuel tanks is a known problem, resulting in major time-consuming maintenance procedures and, in severe cases, can lead to safety accidents and incidents. There are several ways of controlling microbial contamination levels in which the primal one being regular fuel tank bleeding. Our Organization performs daily fuel bleedings on most of its aircraft models to mitigate microbial contamination problems. With a high availability, large fleets, daily fuel bleeding is an expensive procedure from work-load perspective, thus the incentive to decrease the frequency of bleeding regime. Our research investigates experimental procedure for determining the effectiveness of daily bleeding on the occurrence and severity of microbial contamination as opposed to weekly bleeding. The experimental procedure investigated can be used as rigorous scientific tool for determining a lower fuel bleeding frequency, without compromise microbial contamination control. Three types of aircrafts were divided into two populations each, those performing daily and weekly bleeding regimes, respectively. The amount of colony forming units was measured in the two populations in the beginning of the experiments and after about one year. Then, two-part model hypothesis test as proposed by Lachenbruch (1976) was applied on the data, including post-hoc power calculations. A statistically significant difference was found in one type of aircraft, while samples from the two other types were determined as not having enough power to draw significant conclusions, in those cases a proper sample size was determined using numerical simulations. A short discussion of engineering significance of the conclusions is also provided.

AVIATION FUELS PROBLEMS AND SOLUTION - CHAPTER 14 - RESEARCH TEST METHODS FOR CONTAMINANTS IN AVIATION FUELS

Konstantin Tartakovsky, Dr. Regina Sinelnikov, Dr. Moshe Rabaev

Fuel contamination is a catch-all term for anything that causes a fuel test to fail quality assurance testing. Aircraft fuel contaminations are dangerous and may lead to aviation safety accidents and incidents. Fortunately, most contaminations can be detected via simple and quick tests. Contaminants that cannot be detected by standard tests, which usually pose an immediate hazard, will be discussed in this chapter. Inability to detect such contaminants can cause irreversible damage to the fuel system and engines. Understanding the nature and source of the contamination can prevent its reoccurrence, help pinpoint a problem within the fuel system before it becomes critical, and treat the contamination. We will demonstrate that to accurately and effectively identify the pollution and its source, a combination of three working groups is required: a fuel laboratory, a fuel systems engineer, and an analytical research laboratory.

GAINING A DEEPER UNDERSTANDING OF FUEL CHEMICAL COMPOSITION IN THE CONTEXT OF POLAR COMPOUND EXTRACTION PROCESSES

Grant S. Ochoa, Matthew C. Billingsley, Robert E. Synovec

Kerosene-based jet and rocket fuels such as Jet A, JP-8, RP-1, and RP-2 are ubiqitous to the aerospace propulsion industry. There is an ongoing need to more fully assess fuel composition (i.e., specific chemical compounds and compound classes present as a result of refining and feedstock blending) for the purpose of improving quantitative connections between fuel composition, properties, and system performance. While it is well known that polar compounds such as oxygenates play an important role in thermal performance, a deeper understanding of the analytical methods used for their characterization is warranted. Solid phase extraction (SPE) is often employed in laboratory research to target analysis of polar compounds present in fuel. Treating fuel samples with SPE facilitates removal/analysis of specific compound classes depending on the selected stationary phase (e.g., silica or alumina), allowing for the creation of an altered “pass” sample, identical to the original “neat” sample except for the extracted polar compounds. The subsequent methanol extract from the SPE cartridge removes the polar compounds to produce an “extract” sample. These three samples (neat, pass and extract) are then analyzed by comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS) followed by comparative analysis *relative to each other* using tile-based Fisher ratio (F-ratio) analysis, a powerful software tool used to discover chemical differences between the three samples. F-ratio analysis of the neat samples compared with the pass samples provides a global discovery of all compounds affected by the SPE procedure, while the SPE extract sample chromatogram serves as a validation template to assess and ensure that all compounds extracted are accounted for in the comparative analysis. If and/or when the SPE extract sample chromatogram contains fewer analyte peaks than are discovered by the F-ratio analysis of the neat samples compared with the pass samples, this is indicative of analytes that are not removed from the SPE cartridge in the solvent extraction step. Such analytes that are too strongly held on the SPE adsorbent are missing in the extract sample so information regarding their presence in the neat fuel is missed by standard use of SPE sample methodology, compromising the chemical information provided by the analytical methodology. This research has significant ramifications for providing an accurate assessment of the polar compounds present in fuels, which is essential to confidently relate fuel composition to thermal performance.

INVESTIGATION OF SUSCEPTIBILITY OF SYNTHETIC AVIATION FUELS TO MICROBIOLOGICAL GROWTH

Graham Hill, Gareth Williams

Microbial growth in aircraft fuel tanks and aviation fuel distribution systems can cause problems of filter clogging, malfunction of fuel quantity indicator systems and airframe corrosion and can have a dramatic impact on fuel quality and operating safety. Microorganisms can utilise nutrients in any free water present in the tanks, but the hydrocarbon of the fuel provides the principal nutrient for proliferation. Any changes in chemical composition of fuels can thus influence the rate and extent of microbial growth which occurs. Relatively little research has been published on the susceptibility of synthetic and sustainable aviation fuels to microbial growth.

This paper describes a laboratory investigation of the relative susceptibilities to microbial growth of four synthetic jet fuel blends; a coal to liquid (CTL) fully synthetic jet fuel, a gas to liquid (GTL) Fischer Tropsch synthetic paraffinic kerosene and the GTL with blends of 50% naphthenic cut and 20 % hexanol. Susceptibility to microbial growth was compared to a conventional MEROX treated Jet A1. The study utilised laboratory microcosms simulating tanks containing fuel and very small amounts of pure water which were assessed visually and by various microbiological methods over a 2 month period. All fuels, except the GTL blend with 20% hexanol, were found to be susceptible to some degree of microbial growth. The most susceptible fuel was MEROX treated Jet A1, and GTL with 50% naphthenic cut was the susceptible of the synthetic fuels.