

**14TH INTERNATIONAL SYMPOSIUM ON STABILITY,
HANDLING AND USE OF LIQUID FUELS
Charleston, South Carolina USA
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Abstract Summaries

Keynote Address:

**THE FUTURE FOR MARINE FUEL - WHAT'S DRIVING THE ENERGY MIX AND
OUTLOOK FOR DEMAND IN SHIPPING**

Mark Darley

The global shipping industry primarily uses heavy fuel oil for its propulsion requirements. But with local SOX and NOX emissions compliance areas already in force in North America, Northern Europe and Hong Kong and global requirements on the way, the industry is considering its compliance options. These options primarily include use of scrubbers, switching to distillates or LNG. In addition, fuel efficiency and greenhouse gas targets mandated by global regulation are driving change that could even confront today's reality of a total reliance on fossil fuels. In 2014, Lloyd's Register and University College London (UCL) released Global Marine Trends 2030, a report into scenarios for future marine fuel demand. The report provides insight into future fuel demand for the containership, bulk carrier/general cargo and tanker sectors – representing approximately 70% of the global shipping industry's fuel demands. The presentation will build on the GMFT 2030 scenarios to explain the technology challenges and potential options for shipping as the industry gets ready for future change.

John D. Bacha Award of Excellence Paper:

**MEGA-SUPRAMOLECULES FOR SAFER, CLEANER FUEL BY END-ASSOCIATION
OF LONG TELECHELIC POLYMERS**

Ming-Hsin Wei

Liquid fuels, such as gasoline, diesel and kerosene, are the world's dominant power source, representing 34% of global energy consumption. Transportation relies on such liquids, presenting the risk of explosive combustion in the event of impact, such as the 1977 Tenerife airport disaster—an otherwise-survivable runway collision that claimed 583 lives in the post-crash fireball. The UK and the U.S. responded with a multi-agency effort to develop polymeric fuel additives for “mist control.” Ultra-long, associative polymers (e.g., ICI's “FM-9,” >3•10⁶ g/mol copolymer, 5 mol% carboxyl units) increased the drop diameter in post-impact mist, resulting in a relatively cool, short-lived mist fire. However, the polymers interfered with engine operation, and their ultra-long backbone—essential for mist control—degraded upon pumping. They were abandoned in 1986. Fifteen years later, the post-impact fuel fireball involved in the collapse of the World Trade Center motivated us to revisit polymers for mist control. Building on recent advances in supramolecular assembly as a route to emergent functional materials,

particularly assembly of complex polymer architectures, we discovered an unexplored class of polymers that is both effective and compatible with fuel systems. Here, we show that long ($>4 \cdot 10^5$ g/mol) end-associative polymers form “mega-supramolecules” that control post-impact mist without adversely affecting power, efficiency or emissions of unmodified diesel engines. They also reduce turbulent drag, hence, conserving energy used to distribute fuel. The length and end-association strength of the present polymers were designed using statistical mechanical considerations. In comparison with ultra-long polymers for mist control, the present polymers are an order of magnitude shorter; therefore, they are able to resist shear degradation. In contrast to prior randomly-functionalized associative polymers, these end-associative polymers also avoid chain collapse. We found simple carboxylic-acid/tertiary-amine end- association to be effective, and the unprecedented length of these telechelic polymers to be essential for their potent rheological effects.

SESSION 1: RENEWABLE FUELS

FUEL CLEANLINESS – THE SOURCE AND FATE OF CONTAMINANTS FROM REFINERY TO AIRCRAFT

Alisdair Clark

Each day approximately 5 million barrels of aviation fuel flows through the global refining and distribution network to power over 95,000 flights transporting more than 8 million passengers across the globe to link the peoples of the world¹. To ensure long term aircraft and engine reliability fuel cleanliness is paramount. To meet this goal the Aviation Industry have developed stringent specifications and guidelines. In this paper a detailed study of fuel cleanliness is undertaken. The journey travels from large particles of more than 40 microns which the eye can see, through particle sizing technology of 4 microns and Millipore of 0.8 microns, down to submicron material at the very limits of analytical detection. What type of materials are in aviation fuel? Where do they come from and where do they go? An experimental study covering the supply chain from refinery to aircraft, using a range of analytical techniques, seeks to offer insight and understanding.

SUMMARY OF HPCR DIESEL INJECTOR WEAR RESEARCH AND THE IMPLICATIONS OF ADEQUATELY FILTERING FUEL

James Doyle, Matthew Goertz PhD, Scott Grossbauer

In two separate industry cooperative studies, Southwest Research Institute and various participants performed extensive testing to determine the particulate protection/ filtration needs for unit injectors completed in 1999, and again for high pressure common rail injections systems in 2010. Diesel fuel injections systems were challenged with various very narrow distribution dusts to determine the minimum dust particle size that needed to be prevented from passing through fuel injectors. The early testing was done on engine systems and the second round was completed on an actual HPCR fuel system off engine subjected to typical on-engine flow and vibration conditions. The later round of testing demonstrated the extraordinary change in real

world filtration efficiency needed to ensure trouble free operation of HPCR fuel systems. Real world implementation of this high efficiency fuel filtration has exposed new filterable solid sensitivities within typical real world fuel parameters and practices. The intent of this presentation is to briefly describe the new requirements and focus on the filtration challenges and changes needed to run these systems reliably. The change in filtration need amplifies the amount of solid material that needs to be collected in bulk and on-engine many fold. The materials being collected have also changed to now include many fuel insoluble materials that previously contributed to various injector deposits or were simply burned in cylinder.

GLYCERIN RELATED PREMATURE PLUGGING OF FUEL FILTERS

Matthew Goertz PhD, James Doyle, Andrew Dallas PhD, Scott Grossbauer

With the introduction of the Energy Policy Act of 2005, there has been an increasing usage of biodiesel across the United States. The growing usage of these renewable fuels has created several challenges related to filtration. Foremost of these challenges is the removal of residual glycerin from both neat biodiesel and biodiesel blends. Glycerin is a byproduct of the transesterification process used to treat biodiesel feedstocks and is partially removed from fuel through coalescence, centrifugation, and water washing. Over the last ten years Donaldson scientists have investigated several hundred fuel filters that exhibited premature plugging in applications of biodiesel filtration. These filters were from all major manufacturers, constructed of typical fiber materials (glass, cellulose, polyester), and were found to have been extensively fouled with insoluble free glycerin. In this report we detail that biodiesel fuels produced to meet or exceed current standards can still precipitate insoluble glycerin when cooled or when blended with ULSD. We also demonstrate that precipitated glycerin can cause significantly reduced life of fuel filters. Note that all references to glycerin in this report are specific to free glycerin and not alkyl glycerides.

LIGHT OBSCURATION PARTICLE COUNTER FUEL CONTAMINATION LIMITS

Joel Schmitigal

The United States Army conducted a survey of over 1200 fuel samples with the objective of evaluating the proposed limits for use by automatic light obscuration particle counters for the monitoring of aviation fuel cleanliness. The laboratory data collected supports the proposed ISO code limit, based on ISO 4406, of 19/17/14/13 limits for the 4 μ m(c)/ 6 μ m (c)/ 14 μ m (c)/ 30 μ m (c) size channels. The proposed limits were derived from 1.0 mg/L concentration levels for ISO 12103-1 A1 Ultrafine and ISO 12103-1 A2 Fine test dusts, and down to a 5 ppm free water contamination. Based on this work the Department of Defense Tri-Service Petroleum, Oil and Lubricants Technical Steering Committee has recommended these limits for inclusion into Table I of MIL-STD-3004.

ORIGIN AND STRUCTURE OF FUEL DEGRADATION PRODUCTS FOUND IN ULSD AND BIODIESEL

S. Kyle Sontag, Matthew Goertz, Brad Hauser¹, Davis Moravec, Joe Block, and Andrew Dallas

High efficiency fuel filters nearing end-of-life contain two main categories of contaminants: hard particulates and soft particulates. In the soft particulate category, fuel additives and fuel degradation products are commonly observed on returned fuel filters. Fuel degradation products (herein referred to as FDPs) are known to form in the high-pressure common rail of diesel engines, where injection pressures required exceed 40,000 PSI. These high pressures, combined with extreme temperatures often exceeding 200 °C, provide optimal conditions for radical-based degradation of diesel fuel. To investigate the structure and formation of FDPs, Ultra Low Sulfur Diesel (ULSD) was aged in a controlled laboratory environment. The resulting precipitates were collected and analyzed using various spectroscopic techniques, including Nuclear Magnetic Resonance, Fourier Transform Infrared Spectroscopy, and Gel Permeation Chromatography. Furthermore, key components of ULSD suspected to contribute to degradation of fuel are methyl linoleate (a partially unsaturated FAME) and alkyl naphthalene. These precursors were studied in detail through simple model reactions in decane. The degradation products formed in these simple model reactions mimic exactly those found from ULSD aging, emphasizing the problematic nature of methyl linoleate and alkyl naphthalene at high temperatures in diesel fuel. Proposed mechanisms involving radical-based chemistry will also be discussed.

SESSION 2: FUEL PROPERTIES & EFFECTS

RELATIONSHIP OF SMOKE POINT TO JET FUEL HYDROCARBON CONSTITUENTS

David J. Abdallah, Lauren E. Kreno, Caitlin D. Gottier, Gary Christensen, Scott K. Berkhou

Smoke point has been used since the 1930s as a measurement of fuel burning quality. Smoke point is defined as the flame height, under defined conditions, above which smoking occurs. A high smoke point value indicates better burning quality. Jet fuel specifications include a smoke point requirement to control jet fuel burning quality because it correlates to radiant heat transfer in turbine engine combustors and thus relates to combustor life. Only recently, with the introduction of a new automated smoke point apparatus that uses imaging analysis of the flame, has the ability to discriminate smoke point values to 0.1 mm precision levels been possible, a vast improvement over the 1 mm capability of the original subjective manual instrument. The tendency for jet fuel to smoke is related to the hydrocarbon composition. Double GC has made accurate compositional analysis more routine. Combining the double GC data with precise smoke point analysis we have established improved empirical relationships that take into consideration alkyl branching. We have also explored the smoke point tendencies of many neat compounds to better understand the role each plays in smoke point determination.

THE EFFECT OF WATER ON JET FUEL ADDITIVES PERFORMANCE

Paul M. Rawson and Dr. Dietmar Posselt

Aviation fuel additives provide improved performance and enhancement of fuels stability, static dissipation, lubricity and thermal stability. Additives normally provide these enhancements at very low concentrations in the bulk fuel and the impact of water slugs on these normally polar additives requires investigation. Fuels were dosed with a range of individual additives and their performance examined pre and post mixing with water. This mixing was to simulate a large slug of water which may be encountered during fuel handling and distribution. Fuels conductivity, thermal stability, storage stability and lubricity were examined over a range of four jet fuels of different ages and refining process.

LUBRICITY OF RENEWABLE DIESEL FUEL BLENDS

W. Stuart Neill, Jennifer V. Littlejohns, Annie-France Carrier, Simon Lafrance and Ken Mitchell

Renewable diesel is a hydrocarbon blending component option available to fuel suppliers to meet the current renewable fuel regulations in North America, while offering a potential pathway to lower carbon diesel fuels in the future. In this study, the lubricity of renewable diesel fuel blends was investigated with ester- and monoacid-type lubricity improver additives following the ASTM D6079-11 test method. Appropriate lubricity improver additive treat rates were established for the base fuel, an ultra-low sulphur diesel fuel derived from oil sands sources, using the high-frequency reciprocating rig (HFRR). Then, 10, 20, 30 and 50% renewable diesel and winter-grade diesel/jet components were blended with the base fuel using the same lubricity additive treat rates required for the base fuel. The experimental results show that the HFRR wear scar diameter increased for the higher renewable blend percentages for both lubricity additive types. The wear scar diameter increase was more significant for the renewable diesel fuel blends with the ester-based lubricity improver additive. This may be related to the observation that the ester-based lubricity additive was not completely miscible with the base fuel or the renewable fuel blends. A significant fraction of the higher-level renewable fuel blends containing winter-grade diesel/jet components was found to evaporate during a lubricity determination, which effectively increased the lubricity improver additive treat rate. The HFRR wear scar diameters were larger when the gasoline conversion kit was used to measure the lubricity of the more volatile diesel fuels. This suggests that a factor of safety should be used when employing the high-frequency reciprocating rig to measure the lubricity of more volatile fuels.

IMPACTS OF THE JET FUEL CHEMICAL COMPOSITIONS ON O-RING POLYMERS

Mickaël Sicard, Jacques Ancelle, Sandrine Guérin, Bruno Raepsaet, Frédéric Ser

In ASTM D4054 standard, material compatibility tests belong to the Fit-for-Purpose Properties. The aim of these tests is to verify compatibility of alternative jet fuels with materials found in aircraft fuel tanks, fuel systems, and engines. Back-to-back tests were performed on alternative jet fuels and a control sample consisting of a jet fuel. The purpose of the control sample is to provide a baseline for comparison. Test conditions are imposed in the standard. The non-metallic

materials are soaked in the fuels under evaluation for typically 28 days but at various temperatures. After the period, mechanical tests like tensile strength, elongation and volume swell are performed. The results obtained for the materials soaked in alternative jet fuels are compared with those obtained with the materials soaked in the jet fuel reference. These tests are very important, from a technical point of view, in the certification process of new alternative jet fuels as they give a “go-no go result”. Nevertheless, they have a main drawback: they do not explain why the material fails and what happened to it. Obviously, it was the aim of this work to try to understand the fuel impact on the non-metallic materials. In the ASTM research reports, the rate of aromatic compounds was highlighted as one of the most important parameters. Thus, a mandatory limit of 8 % was chosen. In our study, 5 fuels with aromatic rates from 2.5 up to 20.6 mass % were prepared and 3 O-ring types (nitrile, fluorosilicone and fluorocarbon) from the ASTM material list were selected. The test procedure described in the ASTM D4054 was followed. In addition to the standard 28-day soak period, a longer test (125 days) was also performed. After that, the mechanical properties of the O-rings were evaluated through hardness, tensile strength, elongation and volume swell tests. But, additional tests and characterizations (density, XRD, SEM...) were performed in order to highlight the chemical and structural modifications suffered by the gaskets. Moreover, the liquid phases were collected and analyzed by GC, FTIR, particles counting measurements. The results show that the nitrile O-rings are the most affected by the fuels. New chemical compounds and particles were observed in the fuel liquid phase. Moreover, the O-ring density was modified showing evidence of a structural change.

COLD FLOW PROPERTIES OF DIESEL FUELS IN NORTH AMERICA, 2006-2014: GETTING BETTER OR WORSE?

J. Andrew Waynick, Kyle McKee

Over 5,000 diesel fuel samples taken throughout the continental United States and Canada were tested for Cloud Point, Pour Point, and Cold Filter Plugging Point. Samples taken spanned the nine years from 2006 through 2014. The resulting data was evaluated both globally and regionally to determine trends in distillate fuel cold flow properties from the time that ULSD was first introduced until the present.

AVIATION TURBINE FUEL PROPERTIES BASED ON HYDROCARBON TYPE AND SIZE DISTRIBUTION

Zachary J. West, Matthew D. Evanhoe, Milissa M. Griesenbrock

Current aviation turbine fuel specifications place boundaries on key chemical, physical, and performance parameters to ensure fuel quality. Traditionally, satisfying these key points also ensured the fuel was fit-for-purpose. Yet the traditional boundaries established by the specifications are at risk of being incompatible with emerging, but viable, hydrocarbon fuels derived from alternative sources. Some of these issues are due to the nuance in experimental methods, while other issues involve the re-imagining of what an acceptable/appropriate boundary should be. Either way it is desirable to estimate fuel properties based on their detailed composition. We outline a methodology for estimating various fuel properties, e.g., density,

viscosity, speed of sound, and surface tension, as a function of both temperature and fuel composition. A semi-theoretical model, i.e., corresponding states principle (CSP), is extended to an initial set of 52 jet fuels (selected from the CRC world fuel survey) to challenge the method for complex mixtures. Compositional information was derived from GC×GC analysis of each fuel and used as the model input. Initial results indicate model predictions within at least 10% (relative) or better of experimental property values for most quantities. Additional improvements to current models and methods are proposed.

SESSION 3: FUEL TESTING & TEST METHODS

VALIDATION OF EI 1535 3RD EDITION WATER MAPPING PROTOCOLS

Keri Petersen, Gary B. Bessee, Dr. Anthony Kitson-Smith, and Martin Hunnybun

EI 1583 3rd Edition provides alternative methods for screening additives that maybe in other fuels in a multi-product pipeline that could trail-back into the aviation fuel and possibly cause water separation issues downstream. Two protocols were evaluated as potential screening tools with seven (7) CI/LI additives that are currently approved for use by the industry. The water separation characteristics were compared with an industry standard to determine if the water removal was better or worse than the industry standard. Both protocols and test results for the various additives will be presented in this presentation.

ELLIPSOMETER A SUPERIOR METHOD FOR ANALYZING D3241 HEATER TUBE DEPOSITS

Michael C. Croudace, James Hepp, and Olaf Mollenhauer

In the history of jet fuel testing, Jet Fuel Thermal Oxidation Stability Testing ASTM D3241 and IP 323, has always been one of the critical tests for determining fuel safety. If a jet fuel is unstable to thermal oxidation the fuel can deteriorate the performance of the jet engines as deposits are formed the jet engine fuel injectors. These standard tests have been found to be excellent ways to determine the relative stability of the fuel. Unfortunately, the method for determining the relative amount of deposits formed during the test is by visually comparing the depth of color from these deposits which make the results highly subjective. New methods for analyze deposits on heater tubes have been proposed over the years including florescence, interferometer and ellipsometer methods. The history and features of each of these methods will be discussed. The conclusion is that ellipsometer proves to be the superior method for deposit analysis. Ellipsometers produce accurate deposits measurements on any type heater tube with any form of heater tube deposit. The paper examines the current state of ellipsometers instruments and ideas for future developments.

COMPARISON OF JET AND DIESEL FUELS USING CLASSIC AND NEW WORLD OXIDATIVE STABILITY TESTS

David J. Evans

Middle distillate fuels have migrated from high sulfur fuels rich in natural antioxidants down to ultra-low sulfur fuels that have undergone significant hydroprocessing. In addition to this jet and diesel fuels are now being blended with Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK), hydrogenation of esters and fatty acids (HEFA) or hydroprocessed fermentation products. These combinations result in a greater reliance on synthetic antioxidants especially in applications where storage stability is important. Whilst the fuels are changing so too are the methods used to assess the stability of a fuel towards oxidation. Current storage stability tests such as ASTM D2274 and D5304 are well established however new technologies such as the new world methods such as the rapid small scale oxidation test (RSSOT) and quartz crystal microbalance (QCM) are now available. ASTM D2274 and D5304 are carried out at less than 100 °C compared to the QCM and RSSOT which are performed at 140 °C. This paper assesses the current storage stability methods for a range of jet fuel and diesel fuel blends versus the new world methods such as the rapid small scale oxidation test (RSSOT) and quartz crystal microbalance (QCM).

A NOVEL MULTIPLEXED TWO-DIMENSIONAL GAS CHROMATOGRAPHIC APPROACH FOR IMPROVED FUEL ANALYSIS

Thomas N. Loegel, Kevin J. Johnson, and Robert E. Morris

Comprehensive GCxGC-MS couples two chromatographic columns with orthogonal selectivities to a fast Time-Of-Flight (TOF) mass analyzer. This approach enables direct analysis of complex organic mixtures without the need for liquid-liquid extraction pretreatment. The increased peak capacity and selectivity afforded by GCxGC are highly applicable to chemometric analyses. Like all separation techniques, the analysis of complex mixtures using GCxGC-MS is a compromise between high resolution and speed. In order to maximize chromatographic resolution to extract detailed information from a fuel sample, long primary columns are typically used with slow temperature programming. However, as with all chromatographic separations, there are limits to how well co-eluting compounds can be resolved, and this situation is exacerbated by the complexity of hydrocarbon fuels. In order to overcome these limitations, a novel parallel column GCxGC-MS configuration is being developed that will take advantage of multivariate analysis to extract discrete analyte peaks from poorly resolved chromatograms. To accomplish this goal, a LECO GCxGC-TOFMS has been modified to provide two parallel complementary sets of secondary GCxGC columns connected by a capillary flow splitter between the primary and secondary columns. The effluent from both column sets is then combined at the mass detector. In this manner, each analyte in the two-dimensional chromatogram will be represented by two peaks, thus providing a multiplex advantage that can be used in the multivariate analysis to not only isolate poorly resolved compounds, but improve compound identification and quantitation.

THE FUEL COMPOSITION AND SPECIFICATION TOOL (FCAST): A GC-MS MODELING APPLICATION FOR FUEL CHARACTERIZATION

Robert E. Morris, Mark H. Hammond, Jeffrey A. Cramer, Kristina M. Myers, Thomas N. Loegel, Kevin J. Johnson and Iwona A. Leska

A novel data abstraction methodology that enables the use of two-dimensional chemometric modeling to predict fuel properties from Gas Chromatography-Mass Spectrometry (GC-MS) data was described at the 13th IASH Symposium. This methodology was implemented in the form of the FCAST, software intended to serve as a specification compliance screening tool. With the inclusion of new capabilities, the FCAST has been expanded upon and transformed into a versatile analytical tool to characterize, blend and compare fuels through the modeling of GC-MS data. One of the capabilities of the FCAST is the construction of a compositional profile by compound class. Mass spectrometry is known to respond in a non-linear fashion to different hydrocarbon classes, due to differences in ionization efficiencies. We have overcome this limitation by empirically developing a two-factor calibration strategy for the different compound classes found in fuels, enabling the compositional profiles to be reported in mass percent. The means to mathematically blend two fuels and predict the properties of the resultant blends has also been developed and implemented in the FCAST. This provides the means to estimate the specification compliance of different binary blend ratios of two fuels, such as an alternative fuel with its petroleum counterpart. We have also investigated two methods for comparing two fuels through the analysis of GC-MS total ion chromatogram (TIC) profiles. One method operates on the area-normalized TICs and elucidates compositional differences by testing each peak against the standard deviation of the peak differences across all retention times. The other method is based on an analysis of variance (ANOVA) Fisher Ratio analysis, which we described at the 8th IASH Conference. The latter method has been improved upon and implemented in the FCAST to enable the detailed comparison of two fuels.

IGNITION CHARACTERISTICS OF FUELS IN A NEW CONSTANT VOLUME COMBUSTION CHAMBER

Philipp Seidenspinner, Dr. Thomas Wilharm

The ignition characteristic has always been one of the key parameters of diesel and gasoline fuels. Today it plays a decisive role for engine-out emissions and fuel efficiency of vehicles. Unfortunately this important fuel characteristic is still defined by a more than 60 year old technology, based on the use of prechamber combustion engines. When speaking about diesel fuels, the resulting parameter of these combustion engine tests is called Cetane Number (CN) and is defined in ASTM D613. The method's accuracy is highly dependent on skilled engine operators and its use requires up to 1 liter of fuel for a single test run. As an alternative to these engine tests, constant volume combustion chambers (CVCC) have been introduced to determine a Derived Cetane Number (DCN). But these CVCCs are no longer calibrated with the engine's primary reference fuels (PRF). They depend on correlation equations to the engine tests. Therefore a new constant volume combustion chamber has been designed to combine the advantage of a PRF calibration similar to the engine with the benefits of a modern technology CVCC. The latter comprises fast, accurate and fully automated measurement, resistance against non-lubricating substances and solvents, high fuel injection pressures up to 1200 bar and a total

of only 40 ml of fuel needed for a complete test run. Besides, the new CVCC can be heated up to 1000 K inside temperature and pressurized up to 50 bar. This enables the analysis of fuels, even with a low self-ignitability, under engine-like conditions. In a first robustness study with common diesel fuels the new instrument showed a good repeatability of 0.7 CN and an excellent reproducibility of 0.9 CN. All instruments for this study have been calibrated with 6 primary reference fuel mixtures with cetane numbers from 35 to 70. Besides common diesel fuels, methanol, ethanol and gasoline fuels in a cetane number range of 15 and lower have been measured successfully with the direct PRF calibration. Jet fuels, vegetable oils and possible next generation oxygenated diesel fuels have also been analyzed in the new CVCC with a direct correlation to the engine's primary reference fuels, n-hexadecane and 1-methylnaphthalene.

IDENTIFICATION AND QUANTITATION OF POLAR SPECIES IN LIQUID TRANSPORTATION FUELS BY GCxGC

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

Although typically present in trace quantities (ppm levels) in jet and diesel fuels, heteroatomic species have been shown to adversely affect certain fuel properties such as thermal oxidative and storage stability. Identification and quantitation of these polar species is challenging due to the complex hydrocarbon matrices of most fuels. Various attempts have been made to speciate and quantify polar compounds using methods such as high-performance liquid chromatography (HPLC); however, the results tend to be semi-quantitative. Two-dimensional gas chromatography with simultaneous flame ionization and mass spectral detection (GCxGC-FID/MS) has been shown to accurately quantify “non-polar” hydrocarbon types in various fuels.[1] The current work demonstrates a method that employs an initial pre-separation step, using solid-phase extraction, to selectively separate polar compounds from the fuel matrix. This is followed by GCxGC-FID/MS analysis for identification and quantitation of the corresponding polar species classes (e.g., phenols, indoles, carbazoles). The method can be applied to various types of fuels, including those that have been thermally stressed or aged. The accuracy and precision of the application of this method will be addressed.

A REVIEW OF DIESEL FUEL STABILITY TEST METHODS (1930's TO TODAY)

Steven R. Westbrook

This paper is a review of diesel fuel stability test methods. It covers the years since the testing of diesel fuel stability started in the first half of the 20th century up through today. The paper also includes a review of stability tests for fatty acid methyl esters (biodiesel) and biodiesel blends, as they are now common in the diesel fuel market. Test methods for oxidative stability and thermal stability characteristics are included. The origins and evolution of some of today's more well-used methods are discussed. There is also discussion of methods that have come and gone over the years. Information regarding the correlation of test results, where available, is presented and discussed.

A NOVEL SMALL-SCALE WATER SEPARATION INSTRUMENT, WSI

Alan J. Fougere, Ian Mylrea, and Paul Spitteler

D-2 Incorporated along with Stanhope-Seta has developed a new instrument for Small Scale Water Separation determinations consistent with the current ASTM Test Method D3948. The current small scale separator listed in the Method ASTM D3948 was originally introduced in the 1970's and has recently been plagued with poor repeatability & reproducibility in the ASTM inter laboratory cross check program. The new fully automated sensor and sample handling system that uses a novel detector along with new 5th Edition API Filter materials has been shown to improve consistency of ASTM 3948 results. In June 2015 an ASTM task force completed an Inter Laboratory Study (ILS), data from the ILS program, data methods, and, r & R established by that data will be presented, along with overview of the proposed new ASTM method based on the WSI instrument.

SESSION 4: FUEL PRODUCTION, QUALITY & CONTROL

JET FUEL PRODUCT QUALITY – DRIVERS FOR CHANGE

Joanna M. Bauldreay

Jet fuel product quality (PQ) is always under pressure to change – and does, even when the specifications remain unaltered. While most of the interest over the past 10 to 15 years has focused on the approval and introduction of synthetic components, jet fuels are overwhelmingly made from “conventional” feedstocks. They have to meet industry standards, in particular but not limited to the “Table 1” properties of civil and military specifications, and makers of jet fuel are constantly looking at ways to make enough jet fuel and run their operations profitably. EI/JIG Standard 15301 includes a broad overview of jet fuel production and the sorts of measures to ensure that PQ is controlled, but it is a guidance document against which adopters should audit themselves, not a mandatory or “how to make” jet fuel guide. This paper will give an overview of jet fuel production, using both conventional and non- traditional or synthetic feedstocks. It will examine how demands for the major road transport fuels (gasoline and automotive) affect jet fuels, and discuss how refineries are broadening the ways they make jet fuel, such as using new feedstocks and processing technologies. Jet fuel components approved under the ASTM D7566 specification, becoming “drop in” fuels meeting ASTM D1655, DEF STAN 91-91, etc. are adding to the options which can be used to deliver enough fuel to airports, and will also be discussed, but they are unlikely to have a significant global impact until economic measures, expected to be agreed by ICAO in 2016 and implemented after 2018.

PROGRESS TOWARD QUALITY ASSURANCE STANDARDS FOR ADVANCED HYDROCARBON FUELS BASED ON THERMAL PERFORMANCE TESTING AND CHEMOMETRIC MODELING

Matt Billingsley, David Pamplin, Nicholas Keim, Robert Synovec, Benjamin Hill-Lam, and Claire Wilhelm

Ensuring fuel suitability is a challenge faced by propulsion development programs. One common requirement for aircraft, rocket engines, and hypersonic systems alike is effective fuel cooling of engine and vehicle structures, since system performance and reliability depend on the impacts of heat absorption by the fuel. This challenge is exacerbated as operational requirements and fuel chemical makeup extend beyond the historical experience base. These factors increase the necessity for a standardized fuel thermal integrity test and predictive relationships establishing the impact of fuel composition on performance. The Aerospace Fuels Quality Test and Model Development (AFQTMoDev) project is a DLA Energy-sponsored initiative aimed at ensuring operational readiness through fuel quality assurance, ultimately enabling the informed selection of conventional and alternative fuel sources. Specifically, this R&D effort addresses thermal integrity measurement, prediction, and control challenges by developing relevant experimental approaches and implementing state-of-the-art analytical tools to assess and ensure product quality. This presentation will relate technical progress during the first phase of the project, highlighting capabilities of and presenting results from a newly developed compact thermal integrity test method, and describing the application of advanced chromatographic methods and chemometrics to predictive models. Plans for the project's second phase will be previewed in the context of a standardized test methodology for fuel thermal performance and quality assessment.

THE STABILITY, HANDLING, AND OTHER CHARACTERISTICS OF GASOLINE AND DIESEL FUEL PRODUCED FROM END-OF-LIFE PLASTICS

Jay Schabel, and Jeff Trewella, Ph.D.

The liquid transportation fuels market is the largest market in the world, representing over \$2 trillion in revenues on a global basis. The key products gasoline, diesel fuel, jet fuel, and fuel oil are blends that are supplemented with a variety of additives designed to overcome deficiencies (e.g. antioxidants) or impart added benefits (e.g. detergency). The US is a large energy consumer and seeks strategies to enhance its energy security. For example, the Department of Defense views energy security as strategic. Renewable Fuel Standards RFS1 and RFS2 have been enacted in the US to stimulate the renewable fuels industry. End of life plastics are an alternative and abundant feedstock that can be used to produce fungible hydrocarbon fuels that have the potential to significantly enhance US energy security. Initial commercial sales of these fuels are expected to begin in 2016. Based on yields demonstrated at full commercial scale, the amount of fuel that could be produced from US feedstock sources is equivalent to over 7% of today's US refinery crude oil consumption. This paper will present the results of studies aimed at evaluating the product quality aspects of both gasoline and diesel fuel produced from end-of-life plastics. Data will be shown comparing the fuels to their corresponding ASTM standards. In addition, we will share the results of detailed elemental and hydrocarbon analyses that were conducted on these new fuels. Based on all testing to date, both fuels are fully fungible, stable, easy to handle, and have exceptional purity.

ASSURING AVIATION FUELS ARE FIT FOR PURPOSE

Mike Farmery

Clearly, everyone involved in the supply and use of aviation fuel wants it to be ‘fit for purpose’ but exactly what is ‘fit for purpose’ and how do we assure it? Fit for purpose is a term that is often used in the world of retail. We all know when we have bought something that is not ‘fit for purpose’. There is nothing as frustrating as trying to open a bottle of wine with corkscrew that doesn’t work or, even worse, breaks mid-task. Annoying, but at least you can return it to the shop and get your money back. In aviation, fit for purpose must be more than just ‘meeting spec parameters’ because there are examples of fuels that have met the specification values but have subsequently caused operational problems. So, if the numbers are not enough, what is? This session describes the system that has evolved for assuring aviation fuels are fit for purpose wherever they are picked up. It is based on the triumvirate of meeting specification, traceability and quality assurance. Assuring all aviation fuel is fit for purpose wherever it is delivered is absolutely essential; if fuel is causing problems at 35,000 feet half way across the Atlantic, returning it to the airport and complaining is usually not an option.

GLOBAL HYDROCARBON SAMPLING, ANALYSIS AND REPORTS IN THE FORMAT OF WORLDWIDE FUEL SURVEYS

Stefan Sulzmaier

The global fuel world is in constant change and flux. The rate of change has increased over the last few years as a result of many changes in the petroleum world. The retreat of big oil, a geographical shift east and south in the center of gravity of the refining base, the emergence of new technologies and feedstocks as well as a marked fragmentation of the trade network, with new, non technical actors paying an increasing role have all led to a more diverse and complex market. The SGS group and specifically SGS Germany established and runs a global fuel analysis competence centre in Speyer. All aspects of the user experience of fuels are mapped and trends over geographies, time and seasons logged. Fuel analysis has been the single focus of this specialist unit for over 25 years. SGS collects, collates and analyses an enormous amount of data from around the globe through routine bi annual sampling of gas stations, tank farms and refineries. This is carried out at the moment for all kind of fuels such as Diesel, Gasoline, CNG and LNG. These samples are then analyzed in the modern state of the art laboratory in Speyer. The subsequent data produced is then uploaded and built into reports and surveys. The presentation details the main developments in the fuel world over the past two years, some of the main findings and an outlook on future directions.

BEST PRACTICE FOR JET FUEL CONTAMINATION RESPONSE

Marlin Vangsness

Modern aviation fuel delivery organizations do an outstanding job in providing fuel fit for purpose 24-7-365. The Department of Defense, Commercial airlines, NATO, ASME and dozens of other organizations provide guidance on periodic product sampling and testing to ensure that the quality of the fuel is not degraded before aircraft fueling. Guidance for contamination

identification, however, is quite limited. The goal of this study was to propose "Best Practice" procedures to perform as soon as possible after presence of fuel contamination is confirmed. Immediate filter replacement and fuel polishing efforts make finding the source of a contaminate difficult or impossible. Initial steps in response due to QC test failures should include a systematic process to locate the problem source and extent. This study aims to provide sampling, analyzing, and reporting direction to field and laboratory personnel in dealing with unknown contaminants.

USING PRECISION THERMAL STABILITY TESTING TO ENHANCE JET FUEL QUALITY CONTROL AND PRODUCTION

George R. Wilson, III

With the addition of objective heater tube rating to ASTM D1655, the Standard Specification for Aviation Turbine Fuels, there is an opportunity for those who produce and transport jet fuel to take advantage of two decades of research into the formation of fuel deposits that lead to failing the standard test, ASTM D3241/IP 323. This paper presents a model of jet fuel deposition based on what research has shown to be a predictable pattern. With that model explained, the reader is then instructed on how to use this knowledge to monitor Visual Tube Rating efficacy (as the conversion will take an extended period), how to adjust their quality control procedure to provide early notice of process issues before the fuel actually fails to meet specification requirements and when to use stability control additives to ensure downstream quality.

TECHNO-ECONOMIC ASSESSMENT OF THE PRODUCTION OF SYNTHETIC JET FUEL BY ELECTROLYSIS AND FISCHER-TROPSCH SYNTHESIS

Daniel H. Koenig, Ralph-Uwe Dietrich, Antje Woerner

Future aviation will continue to depend on energy carriers with a high energy density. The "Power-to-Fuel" technology is an approach to produce synthetic jet fuels from renewable energy (solar, wind). The German Aerospace Center investigates and evaluates the technical and economic performance of production processes based on these renewable energies and CO₂. One process concept comprises the generation of H₂ by water electrolysis from fluctuating renewable power sources. CO₂ – e.g. sequestered from industrial resources – reacts with H₂ by the reverse water-gas-shift reaction to form syngas. Syngas is then synthesized to long chained hydrocarbons by the Fischer-Tropsch synthesis. The downstream product separation and upgrading section allows the production of gasoline, kerosene and diesel. A flowsheet simulation model of the proposed concept was set up and a pinch point analysis was conducted. The feed capacity was set to 1 GWLHV of H₂ and offshore wind power was selected as the feedstock electricity. The process performance is evaluated by the Power-to- Fuel efficiency, which is the fraction of the total electrical energy input chemically bound into liquid hydrocarbons. A baseline Power-to-Fuel efficiency of 44 % was calculated. The carbon conversion was 73 %. The sensitivity of various operation conditions was analyzed. A Power- to-Fuel efficiency of up to 62 % was found, when a high temperature solid oxide electrolyzer is applied. The higher efficiency is obtained by the use of the process excess heat by the electrolyzer. For systems based on a stationary power input, production cost in the range from 5 \$/GGE to 9 \$/GGE were found. The

production cost range from 12 \$/GGE to 21 \$/GGE when the system is powered by a renewable fluctuating energy source. The sensitivity of the full load hours, electrolyzer capital cost and electricity prices were analyzed and their effect on the production costs will be presented at the conference.

SESSION 5: DIESEL & BIO-DIESEL

USE OF MONO-OLEATE AS A BIODIESEL SIMULANT FOR FUEL WATER SEPARATION

Gary B. Bessee

Diesel fuel-water separation is a major component of protecting the hardware in any engine driven vehicle or machine. Defining the properties of biodiesel for determining the fuel water separation characteristics of a filter is very difficult. Depending upon the type or types of plants and/or animal is used in the production of biodiesel, the fuel water separation properties can vary greatly and create issues with generating repeatable and reproducible test results. In an effort to “standardize” the biodiesel for SAE J1488 and ISO 16332, mono-oleate is being evaluated as a simulant for biodiesel. Various samples of mono-oleates were obtained and evaluated using GCXGC/MS TOF, various rheology and tribological test methods, Malvern laser droplet size determination, and SAE J1488 on two selected filtration systems to determine the variability in mono-oleates and which ones could be considered the “same.” The test results were able to differentiate between the various mono-oleate samples to provide industry with multiple suppliers, while providing important physical, chemical, rheological, and tribological properties. SAE J1488 results confirmed the selected mono-oleates provided repeatable results with two different types of fuel water separation with differing degrees of water separation efficiency. This paper will present the GCXGC/MS TOF results, selected rheological and tribological results, Malvern droplet size distributions, and SAE J1488 results.

AN ASSESSMENT OF THE THERMAL AND OXIDATIVE STABILITY EXIGENCY FOR DIESEL FUELS IN PRESENT ENGINES AND THE SOLUTIONS MOST EFFICIENT FOR EACH SPECIFIC CASE

Delgado, J.; Nieto, A.I.; Castillo, E.

The progressive reduction of sulfur in diesel fuels, the increasing incorporation of fatty acid esters, the presence of metallic contaminants in fuels and the high temperatures of the new injection systems of the engines in European market, are factors that lead to different degradation mechanisms from those expected from a diesel fuel. This instability cause severe malfunctions in engines (blockage, corrosion, deposit formation, a poor fuel injection and a non-optimal combustion). It has been proven presence of metals contents greater than 0.1 mg/kg in European fuels sampled between 2003 and 2014; these contaminants act as initiators and catalysts for oxidation reactions of fuel. The European specification for diesel fuel EN-590 allows a FAME content of 5% since 2004 and till 7% since 2009; this environmentally friendly component incorporates olefins which are highly reactive to oxygen. Finally, the new diesel engines with

fuel injection "common rail" expose to fuels at temperatures above 100°C, favoring the dissolution of metals and the accelerated degradation of the fuel. We have assessed the stability of diesel under specifically developed methods for simulating the new conditions. Several metal deactivators, in different combinations with dispersants and antioxidants, have been used for stabilize the fuel. The most effective combination depends on FAME content and it is also critical the presence of sulfur compounds, which are natural antioxidants but are also insoluble promoters. A suitable dispersant is highly effective for moderate sulfur contents (350 mg / kg); a proper metal deactivator is the most effective for low sulfur fuels (50 mg / kg). The antioxidant is critical to obtain the same effectiveness in stabilizing sulfur free fuel (<10 ppm) or with high content of fatty acid esters.

INVESTIGATION OF RELATIONSHIP BETWEEN WATER CONTENT IN BIODIESELS AND MICROBIAL GROWTH AND CONTAMINATION

Gareth Williams, Leon O'Malley & Graham C. Hill

Previous research sponsored by the Energy Institute demonstrated a positive correlation between the FAME content of biodiesel and its susceptibility to microbial growth. Those studies were undertaken under conditions where excess water was available to promote microbial growth. Compared to conventional fuels, biofuels containing Fatty Acid Methyl Esters (FAME) have increased propensity to hold water. It is suspected this may promote the ability of microbial growth to occur throughout the bulk fuel phase in storage tanks and impede ability of microbial contamination to be removed by routine tank settling procedures. This paper reports further work sponsored by the Energy Institute to investigate the relationship between water content and microbial growth in biodiesels. Microcosms of biodiesel blends (B0, B10 & B20) with varying total (free and dissolved) water contents (100 ppm, 400 ppm, 1000 ppm & 10000 ppm) were inoculated with low numbers of a consortium of fuel degrading microorganisms and held at 21°C and 70% RH for 14 weeks. The diesel microcosms were agitated weekly. At regular intervals, the microcosms were sampled from four depths (dead bottom (fuel phase), lower third, middle third and upper third) and assessed for water content (IP438) and viable microbial content (IP613). At the end of 14 weeks the fuel filter blocking tendency (IP387) and the total acid number (IP177) were assessed. A visual assessment of the amount of filterable biomass present was also conducted. Additionally, one microcosm was selected for a further study to investigate the influence of settling time on the vertical distribution of microbial contamination and water. Results obtained from the study will assist in developing best practice for handling and storage of biodiesels.

FAME IN DIESEL CROSS-CONTAMINATION OF FAME-FREE DIESEL FLOWING THROUGH A 10-INCH PIPELINE

Paul Spitteler, Rod Woodford and Ian Mylrea

A shared distribution network introduces the risk of cross-contamination between different fuels. In particular Fatty Acid Methyl Ester (FAME), which is a surface-active compound, presents a significant challenge to the aviation industry. The maximum FAME cross-contamination allowed in the jet fuel specifications DefStan 91-91 and ASTM D1655 is 50 mg/kg. Other industrial

sectors such as power generation have the need to store fuel for long periods. In power generation, standby generators are used infrequently and they are therefore keen to store FAME-free fuel to avoid fuel deterioration with time. Therefore, it is essential to accurately monitor the levels of FAME cross-contamination for fuels transported through the pipeline. This paper discusses the findings of a study conducted in the USA where a B5 biodiesel blend was transported 266 miles in a 10 inch pipeline. This was followed by a FAME-free Diesel cargo to enable the levels of FAME to be monitored to determine the extent of cross-contamination. The development of a new test method, ASTM D7963 which enables the detection of FAME in Diesel at trace levels within 15 minutes using the FIJI instrument, is described in detail. Samples from the analysed FAME-free Diesel batch typically show a slow general decay in FAME levels. However, deviations from the general downward trend were also observed.

SESSION 6: MARINE FUELS

A GLOBAL SURVEY OF THE INCIDENCE OF FAME AND MICROBIAL CONTAMINATION IN MARINE DISTILLATE FUELS.

Graham C. Hill, Leon O'Malley, Paul Livingston & Timothy Wilson

On 1st January 2015 the sulphur content of marine fuels in use inside Emission Control Areas (ECA) reduced from 1.00% to 0.10%. Ultra-low sulphur automotive diesel which contains Fatty Acid Methyl Esters (FAME) at up to 7%, are already widely used in Europe, USA and other global regions. Given the complex supply chain of marine bunker fuels and the increasing demand for low sulphur gas oil it would seem inevitable some fuel blended with biodiesel will find its way into the marine fuels supply chain. To evaluate the true extent of FAME (biodiesel) contamination in the marine distillate fuels, a joint survey was conducted by Lloyds Register FOBAS, Guardian Marine Testing Ltd (GMT) and ECHA Microbiology Ltd. Nearly 2400 samples of marine distillate fuel derived from wide range of ports, suppliers & barges and considered to represent a good overview of the global market for marine distillates, were tested for compliance with ISO 8217 standard parameters and additionally for FAME contamination, using IR spectroscopy. 116 (4.68%) of the samples were positively identified with FAME and were then tested by the reference EN 14078 method to accurately quantify the level of FAME contamination. All samples which were identified with FAME, along with 32 randomly selected FAME-free samples, were then analysed for viable microbial content (IP 613) and water content by Karl Fisher analysis. A strong correlation between viable microbial contamination and water content was observed. Marine distillate fuel containing FAME was found to be more likely to contain viable microorganisms. Marine fuel containing FAME is more likely to contain a higher level of viable contamination than marine fuel lacking FAME.

NRL-DLA FUEL FORENSICS & F-76 INVESTIGATION

Daniel Baniszewski, Robert E. Morris, Joan Melendez, Pamela Serino and Richard Kamin

Beginning July 2014, US Navy vessels experienced increased filter plugging and frequent changes of fuel filters in the Pacific. Looking at the supply chain, F76 marine distillate product

involved Navy oilers issuing to six or seven customer vessels with turbine engines. Inconsistent sampling and test results from vessel cargo and bunkers tanks indicated darker color fuel with high particulate. Samples were generally clear and bright with no visual sediment, however they apparently have fine particulates and test high for particulate contamination. Results range from within specification of max 10 mg/L, to 30s, 40s, 60s, and up to 200 mg/L. More reliable sampling of the vessel before discharge had on spec particulate contamination near the maximum allowable limit. Subsequent to the above issue, other incidents in the Pacific of high particulates have sporadically occurred on vessels and in storage tanks with product previously showing on specification results. Lastly, it was found in many retain samples on the west coast that “rings” had quickly appeared on the bottom on the containers and many contained particles and sediment as well. Testing has been conducted at both commercial and military laboratories to try and determine if the fuels in question contain constituents that are not characteristic of diesel fuels and diesel fuel adherent gums and/or if particulates/gums are the result of unexpected interactions between approved additives and other normally found constituents in F-76.

OVERVIEW OF U.S. NAVY’S RECENT FUEL QUALITY ISSUES

Joan Melendez, Richard Kamin, Diane Mattingly, John Buffin, and Amy Carico

The United States Navy uses two specialty fuels for shipboard propulsion and naval aviation, NATO F-76 and JP-5 (NATO F-44) respectively. Military applications and readiness necessitates additional requirements for fuel properties and introduces some unique challenges to maintaining fuel quality. This paper will discuss recent fleet support investigations and the methods used to detect and remediate the fuel quality issues. Recent problems have included rapidly degrading F-76 resulting in premature filter clogging and oily waste contamination of JP-5 aboard a ship. Investigations have utilized specification tests as well as analytical instrumentation to determine the type and concentration of contaminants. Remediation efforts were developed to meet mission readiness based upon test data and prior experiences.

OVERVIEW OF U.S. NAVY’S SHIP PROPULSION FUEL (F-76) TEST & QUALIFICATION PROGRAM

Richard Kamin, Joan Melendez, Dr. Ryan Turgeon, and Kristin Weisser

The United States Navy has been evaluating non-petroleum sourced alternative fuels for use as a military fuel replacement. The Navy requires that any alternative sourced fuels be drop-in replacements that require no modification to existing propulsion systems. Various fuels have been tested that include both neat alternative and different percentage blends of alternative / petroleum fuel. Laboratory testing of chemical and physical properties performed on each fuel showed similar or improved properties when compared to petroleum sourced fuels. This testing includes specification, fit-for-purpose, component testing, engine testing, and full scale demonstrations with decision points built in after each stage is completed. This paper will present the current status and results of the US Navy’s program to evaluate alternative sourced fuels in both aviation and diesel.

SESSION 7: FUEL ADDITIVES

SYNTHESIS AND EVALUATION OF GLYCEROL ETHERS AS ALTERNATIVE FUEL ADDITIVES

Nur Bağlar, Fatma Meliz Tunç, İsmail Doğan Günbaş, Serdar Çelebi1 Özge Deniz Bozkurt, Alper Uzun

Di and tri-tert-butyl glycerol ethers are among the emerging oxygenate fuel additives known as biodegradable and compatible with gasoline and diesel. These ethers improve the octane number of gasoline and cold flow characteristics of diesel and biodiesel fuels. The objective of this study is to evaluate the future utilization of glycerol ethers in TUPRAS refineries as alternative oxygenate fuel additives for gasoline and diesel. Di and tri-tert-butyl glycerol ethers (higher ethers) were synthesized via etherification in batch and continuous reactor systems in the presence of commercially available heterogeneous catalysts. Product characterizations were done via GC-MS. In the first part of the study, pure glycerol and isobutylene were used as model feed in etherification reaction with commercial and modified catalysts such as zeolites, ion exchange resins, and mesoporous silicas. High glycerol conversion and high di and tri-tert-butyl glycerol ethers selectivity were achieved with both commercial and modified catalysts. Based on the obtained results, crude glycerol from biodiesel production plant and C4 fractions from the FCC units in TUPRAŞ refineries were used as feed in the second part of the study. In order to test the fuel compatibility of the products, higher ethers were separated from final product and fuel-ether blends in specific proportions were prepared. Then, fuel compatibilities of these blends were tested according to ASTM D4814 and ASTM D975 standards. Results are comparable with commercial fuel additives in terms of octane booster and cold flow improver specialties. This work is financed by The Scientific and Technological Research Council of Turkey.

TESTING OF POPULAR CORROSION INHIBITORS AT COMMON TREAT RATES

Richard L. Chapman and Simon Mulqueen

In recent years, there has been a rise in deposits of various types found in diesel fuel injection systems. These deposits have been seen in filters, injector tips and recently inside injectors. The latter internal diesel injector deposits (IDIDs) have been the subject of a number of recent publications, and are the subject of investigations by various industry groups in Europe and the U.S. Generally, three types of deposits have been identified: carbonaceous and metal carboxylate (primary) and amide lacquers (secondarily). Metal carboxylate salts of hexadecenyl and/or dodecenyl succinic acids (HDSA/DDSA) have been singled out in industry groups as the primary cause for most of the problematic internal injector deposit issues. This focus on succinate salts diminishes the possible impact of other acidic species that can be found in the fuel at much higher treat rates than corrosion inhibitors. These corrosion inhibitors are critically necessary to prevent pipeline, storage tank and end-use corrosion, are typically used at very low treat rates and contain only a fraction of the HDSA/DDSA acids. It is therefore unlikely that they are the main cause of internal diesel injector deposits. This work will describe testing which shows that non-corrosion inhibitor acidic additives at their higher treat rates may cause filter and injector sticking problems while metal salts of HDSA/DDSA corrosion inhibitors at normal treat rates do not.

POTENTIAL PROBLEMS OF HIGH EFFICIENCY FUEL FILTRATION AND COLD FLOW IMPROVER ADDITIVES

Matthew Goertz, Davis Moravec, and Andrew Dallas

Cold flow improvers are a class of fuel additives designed to modify the size and shape of wax crystals formed in fuels below their cloud point. These additives are designed to precipitate at temperatures above the fuel's cloud point and serve as both nucleation centers and wax particle growth arresters. In this study we demonstrate that, under certain conditions, current commercial cold flow improvers formulated with polyethylene-vinyl acetate can directly lead to premature fuel filter plugging. Furthermore, the necessary use of high efficiency filtration to protect modern high-pressure common rail fuel injection systems exacerbates these problems. High efficiency filters tend to capture the wax particles, even those modified with cold flow improvers, that would pass through the more open filters previously used to protect fuel systems. Potential solutions to these problems along with the need to revisit cold weather fuel operability standards will be addressed.

MBO – A NEW MICROBICIDE FOR THE USA FUEL MARKET IN COMPARISON TO CMI/ MI – A WELL ESTABLISHED MICROBICIDE

Andreia Jorge

The active 3,3'-Methylenebis[5-methyloxazolidine], also known as MBO has been widely used in Europe since 1976. It is now available in the USA where a microbicide containing CMI/MI is already broadly used since decades. How are both biocidal actives in comparison in regards of their efficacy against microorganism and their properties as fuel additive in ULSD? MBO can now be used for the US fuel market for treating ULSD. It is free of sulfur and chlorine and provides further physical and chemical properties which are beneficial for the use as a fuel additive. These properties will be compared with the active known as CMI/MI which is a mixture of 5-chloro-2-methyl-3-(2H)-isothiazolone (CMI) and 2-methyl-3-(2H)-isothiazolone. Furthermore the latest ASTM E1259-10 test result shows the efficacy of MBO and CMI/ MI in ULSD in the lowest and highest recommended dose rate.

IMPACT OF DISTRIBUTION SYSTEM ON METAL DEACTIVATOR ADDED TO JET FUEL

Paul P. Wells, Lauren E. Kreno

Metal Deactivator Additive (MDA) may be added to jet fuel to improve thermal oxidative stability with or without proven soluble metal contamination present. In most cases, the MDA will be added to counter suspected contamination. In this instance, some portion of the MDA will be complexed with metal and the remaining portion will be free (assuming the MDA has been added in excess). In other limited cases (i.e. point of manufacture), contamination is not suspected and the MDA is added purely to improve thermal stability. There is little documentation regarding the fate of MDA in the jet fuel distribution system. There is a concern that as the treated jet fuel progresses through filtration and clay treatment that the MDA may be removed. In cases where non-metal-containing fuel was additized to meet D3241 requirements,

the previous poor thermal stability may be restored. Through lab- and test rig-scale studies, the following questions were explored: Will filter monitors remove MDA (either free or complexed)? Will clay adsorb MDA (either free or complexed)? Answers to these questions are crucial for ensuring that additized fuel remains on specification through the supply chain to the aircraft.

SESSION 8: ALTERNATIVE AVIATION FUELS

FUEL MATRIX ANALYSIS USED FOR THE FRENCH PROJECT “CAER” DEDICATED TO THE ALTERNATIVE FUELS FOR AERONAUTICS

Pascale Demoment, Anne Gandubert, Arij Ben Amara and Laurie Starck

CAER is a French project supported by DGAC under the convention n°2012 93 0805. It started in September 2011 and will last four years. CAER gathers a multi-disciplinary consortium composed of 10 members : IFP Energies Nouvelles (Coordinator of the project), CNRS, Dassault, Airbus Group Innovations, INRA, Snecma, Total, Air France, Airbus, INRIA. The members represent key industrial partners from aeronautics (engine and aircraft OEM) and fuel industry, as well as from research organizations covering a large spectrum of expertise in such fields as biochemistry, refinery, combustion, aircraft systems or industrial safety. The objective of the project is to federate French R&D on the field of alternative fuels for aeronautics in order:

- To better understand the different phenomena
- To participate effectively in the international certification process
- To be active in the field of the future production pathways of biofuels

CAER develops an integrated approach “From the production to the impact on the aircraft”. The work that will be presented is the fuel matrix strategy and the characterization of the different fuels used in the CAER project.

OPERATIONAL VOLUMES: RECENT DLA ENERGY ALTERNATIVE FUEL ACQUISITIONS

Pamela Serino and Daniel Baniszewski

DLA Energy has supported the services in their certification and approval efforts through numerous procurement actions. From 2007 through 2014 DLA Energy awarded numerous contracts for Fischer Tropsch, Hydroprocessed Esters and Fatty Acids (HEFA), Alcohol to Jet (ATJ), Synthesized Iso- Paraffins (SIP) (formerly Direct Sugar to Hydrocarbon), and Hydroprocessed Depolymerized Cellulosic Diesel (HDCD) F-76 from various feedstocks to support the certification and approval of these fuels for aviation and marine applications. Recent alternative fuels contracts awarded over the last year for certification and qualification efforts include catalytic hydrothermal conversion diesel (CHCD-76) to and catalytic hydrothermal conversion jet (CHCJ-5).

DLA Energy also supports the transition of these fuels from certification and qualification volumes to operational quantities. DLA Energy is providing technical and potential contracting support to the Department of Energy (DOE), Navy and United States Department of Agriculture (USDA) with their coordinated Bio-refineries Program which aims to partner with industry to create robust domestic production for advanced drop-in biofuels. The ultimate goal of the program is to assist in the financing of constructing several bio-refinery enterprises, each capable of refining in excess of 10 million gallons of cost competitive advanced biofuel blendstock suitable for producing military grade finished fuels, by 2017. Lastly, DLA Energy is lending support to the Navy's Farm to Fleet initiative. This initiative involves Navy requirements for a minimum 10% biofuel blend for JP-5 and F-76 to be supplied in contracts resulting from DLA Energy Bulk solicitations for its Inland East Gulf (IEG) and Rocky Mountain West (RMW) purchase programs. The initiative is utilizing USDA Commodity Credit Corporation funding to defray biofuels feedstock costs so that DLA Energy awards are made at no additional cost to the DOD. A unique aspect of this procurement is that the biofuel blends (JP5 and F-76) will be required to have lifecycle greenhouse gas emissions less than those of conventional petroleum derived fuels in compliance with section 526 of the Energy Independence and Security Act of 2007. Unfortunately, no successful alternative fuel awards were made for this most recent Inland East Gulf solicitation as a result of significant technical issues encountered with the offered F-76 alternative fuel product. There's an inherent misunderstanding and confusion from alternative diesel producers with respect to the requirements of alternative F-76 testing requirements. The proposed product did not meet the F-76 alternative fuels specification in several key areas including carbon & hydrogen content, metals, flash point, particulates, and DSEP. Other logistical issues were encountered that compounded the problem such as insufficient storage to satisfy testing requirements of the neat biofuel. This initiative continues in the current Rocky Mountain West solicitation.

ADVANCES IN ALTERNATIVE FUEL CONTENT MODELING USING NEAR- INFRARED SPECTROSCOPY

Jeffrey A. Cramer, Mark H. Hammond, Kristina M. Myers and Robert E. Morris

Partial least squares (PLS) regression models can be constructed from near-infrared (NIR) spectroscopic data to predict critical fuel specification properties. Implementing such models into the data handling algorithms of small, field-portable NIR equipment would allow for fast in-situ fuel quality surveillance operations. However, the presence of alternative fuels in fuel blends can affect the most fundamental aspects of NIR spectroscopic data and, consequently, adversely affect how well PLS models can predict the fuel properties of these blends. To compensate for this, additional PLS models can be used to predict alternative fuel contents themselves, and the results from these models can subsequently be used to correct the predictions made by the corresponding PLS fuel property models. Several alternative fuel types have been incorporated into a generalized content and property modeling strategy that will be discussed during the course of this presentation. The developed strategy provides the means to allow fuel-based NIR PLS models to predict and quantify alternative fuel contents in blends in a robust fashion that, due to at least some fuel-independent predictive capabilities, better accommodates a future of unknown and unknowable fuel types.

PRODUCTION OF AROMATIC DROP-IN JET FUEL FROM VEGETABLE OILS

*Moshe Rabaev , Roxana Vidruk-Nehemya, Miron V. Landau, Moti Herskowitz**

The catalytic conversion of vegetable oils to green drop-in jet fuel was carried out in mini-pilot trickle-bed reactor. The green drop-in jet fuel produced by our novel process met the specs (ASTM D7566, ASTM D1655) determined by a certified laboratory. Three hydrodeoxygenation routes were identified: (1) hydrodeoxygenation to water, (2) decarboxylation to CO₂ and (3) decarbonylation to CO. Hydrodeoxygenation and reforming of the triglycerides were performed on a proprietary, modified Pt-SAPO-11/ γ Al₂O₃ catalyst in a trickle-bed reactor to produce hydrocarbons with content of 14-16% monoaromatic and >50% isoparaffinic compounds. This stage was followed by fractionation, mild hydrocracking on Ni₂P/HY catalyst and additional isomerization on Pt-SAPO-11/ γ Al₂O₃, to achieve after fractionation >50 wt% of jet fuel with >8% aromatics. Stable operation of the catalytic process was recorded for >1000h on stream, running the hydrodeoxygenation at 375-380°C, 30 atm and LHSV = 1h-1. The hydrocracking and additional isomerization at 300-330°C and 350°C, respectively, 30 atm and LHSV = 1-3h-1. The light and heavy fraction recovered can be further processed to yield gasoline and diesel products.

SESSION 9: MICROBIOLOGICAL

A RISK BASED APPROACH FOR DEVELOPING MICROBIAL MONITORING STRATEGIES FOR FUELS

Graham C. Hill & Anthony Kitson-Smith

Microbial growth in distillate fuel systems can lead to rapidly accelerated corrosion, filter blocking and increased levels of tank contamination requiring more frequent cleaning. It is important to avoid this growth both for the integrity of the operation, and also to prevent contamination from passing downstream, ultimately contaminating end use transport vehicles and electrical generators. Three elements are typically necessary in order to initiate and sustain microbial growth in any fuel system; fuel - used for energy, microbes - that are ubiquitous in the surrounding environment or the result of downstream contamination, and water – that creates and sustains a viable environment for microorganisms to grow and thrive. This paper seeks to provide guidance on appropriate risk-based monitoring strategies for use throughout the distillates fuel supply chain (both aviation kerosene, diesel and gas oil). The focus is to provide guidance and facilitate operators wanting to employ microbial testing as part of their management and control strategy for both fuel product quality assurance and facility maintenance. Where microbial contamination has been confirmed by testing, more detailed monitoring can help identify potential upstream or local sources and provide remediation strategies. As there are no industry specified limits for the manufacture or distribution of distillate fuels up to point of delivery so the risk-based guidance is intended to ensure microbe levels at point of delivery are fit for purpose of the end use of the fuel. Whilst microbes are inherent in most storage and distribution systems, proliferation of microbes requires certain conditions. The industry recognises that good facility design, and for instance, constant daily

draining of storage tank sumps, repetitive filtration of fuel as it moves through the storage and distribution system can significantly attenuate the movement of microbes downstream. In particular, facility design such as lined or partially lined tanks, cone down centre sump tanks, floating suction as well as appropriate water management protocols can help to prevent this proliferation. To facilitate this management of fuel quality, an understanding of the normal background microbial contamination levels in a facility and monitoring for change can provide early warning of potential problems and help prevent expensive and disruptive remediation. This paper proposes the use of “Low”, “Warning” and “Action” levels assessed when using on-site microbiological test kits. Suggested levels are provided for guidance on test kits best suited for testing fuel samples taken from critical control points. The actual levels for Warning (Moderate Contamination) and Action (Heavy contamination) may need to be modified based on location and type of sample, as well as experience gained during the initial background level evaluation screening. However, the extent and frequency of testing should be based on an assessment of risk of microbial growth in the fuel facility. As such, monitoring for change in the background levels, rather than adhering to absolute limits are the key to successful control strategies.

AVIATION FUEL BIODEGRADATION UNDER STATIC CONDITIONS AND IN A STIRRED-TANK BIOREACTOR

Richard C. Striebich, Susan S. Mueller, Linda M. Shafer Thusitha Gunasekera and Oscar Ruiz

In this study, we report on the investigation of bacteria taken from the environment which are useful or important in the degradation of petroleum and alternative jet fuel and diesel fuel in storage tanks or in the environment. These bacteria were studied in small vials with limited amounts of oxygen, in order to screen the suitability of bacteria to treat particular hydrocarbon mixtures. The scale of this process was then scaled to a 5 Liter bioreactor to further investigate remediation applications for jet fuel contamination and tank storage. The bacteria *Pseudomonas aeruginosa*, *Pseudomonas stutzeri*, *Ralstonia picketti* and *Gordonia* sp., were exposed to liquid fuel in the bioreactor. The fuel, oxygen concentrations, biological growth and other parameters were monitored to understand the bacterial degradation of the fuel and the interaction of the bacteria with each other. Results showed that each bacterium consumed specific compounds and would not adapt to consume other compounds in jet fuel. Of the four bacteria investigated, two were found to exclusively consume aromatics, and one of which consumed all of the naphthalene in the fuel within one day. One of the bacterium was effective on branched alkanes in the fuel. The implications for fuel quality and bioremediation are discussed.

A NOVEL APPROACH IN THE USE OF FOOD GRADE YEAST AS A NATIVE STANDARD FOR THE DEVELOPMENT OF PRECISION AND BIAS FOR A RAPID BIOLUMINESCENCE ASSAY METHOD – ASTM D7463 STANDARD TEST METHOD FOR ADENOSINE TRIPHOSPHATE (ATP) CONTENT OF MICROORGANISMS IN FUEL, FUEL/WATER MIXTURES, AND FUEL ASSOCIATED WATER

Edward English

When determining the precision and bias associated with an analytical test method many factors must be identified and considered in order to reduce or eliminate sources of systematic error

resulting in an effective and robust test protocol. This includes sample collection, sample preparation, harvesting the analyte of interest, detecting the analyte of interest, and accounting for sample matrix effects to name a few. In some instances, circumstances may prevail where an analytical test protocol must be validated by inference or by surrogate technique because the analyte of interest is not available commercially or is not easily utilized in its “native” form as found in the field. Such was the case with ASTM D4012 Standard Test Method for Adenosine Triphosphate (ATP) Content of Microorganisms in Water. In this method the author admittedly relied on the analytical grade of the target analyte because it was not available as a workable and stable standard in its “native” form. Now that ATP Bioluminescence Assay has gained wider acceptance for use in the fuel industry, this new microbial analytical technique must be challenged using standards that are as close to the “native” form in the proper sample matrix or matrices. This paper describes a novel approach to utilize a commercially available food grade yeast to research and develop a stable ATP standard that could be utilized in its “native” form in the various sample matrices found in the field so as to challenge the validity and robustness of a ATP Rapid Bioluminescence Assay, ASTM D7463 Standard Test Method for Adenosine Triphosphate (ATP) Content of Microorganisms in Fuel, Fuel/Water Mixtures, and Fuel Associated Water.

SESSION 10: FUEL STORAGE & HANDLING

CORROSION REDUCTION IN ABOVEGROUND ASPHALT STORAGE TANKS

Matthew T. Barnes, Ksenija Babic, PhD

The storage of asphalt or residual oil in carbon steel tanks at elevated temperatures is a common practice that leads to the generation of large concentrations of hydrogen sulfide (H₂S) in the tank headspace. The high H₂S levels (sometimes more than 10,000 ppm in the vapor phase) are caused by the thermal cracking of sulfur compounds inherently present in the oil. These cracking reactions can occur at temperatures as low as 200°F (93°C). The toxic nature of H₂S presents a safety risk to those working around storage tanks, and a hazard to the surrounding environment and communities. Many regulations are already imposed to monitor and reduce exposure to H₂S. The combination of elevated temperatures, high H₂S concentrations and the presence of other corrosive species such as water and salt in humid coastal regions, carbon dioxide and volatile organic compounds, create an aggressive environment conducive to storage tank corrosion. Hydrogen sulfide emitted from asphalt readily dissolves in water, increasing the corrosion potential, which can compromise the integrity of tank roofs. Therefore, the control of H₂S is critical for terminals storing and transporting sour asphalt, from both safety and asset management points of view. The use of H₂S scavengers in field applications is shown to help reduce the rate of corrosion inside asphalt storage tanks by dramatically reducing the H₂S concentration in the tank vapor space. A laboratory test protocol was designed to simulate the asphalt storage tank environment at high temperatures. Asphalt or vacuum tower bottom samples containing elevated H₂S levels were evaluated for corrosion potential on carbon steel. A notable reduction in corrosion was observed when samples were treated with H₂S scavengers. Corrosion data collected following the exposure of mild steel to corrosive asphalt vapors, with and without scavenger treatment, are presented in the paper.

EFFECT OF DIFFERENT DRAINAGE REGIMES ON FUEL MICROBIOLOGICAL CONTAMINATION LEVEL IN COMBAT AIRCRAFT FUEL SYSTEMS

Ella Lam, Nofar Kaslasi, Moshe Rabaev, Joseph Geva, Rephael Fass, Tomer Mevorach, Michal Yardeni

The IAF does not use biocides or anti-icing additives on a routine basis. Therefore, it conducts a continuous tracking on microbiological contamination level in its fuel distribution systems and aircraft fuel tanks. The results serve as an early warning system regarding the possible development of microbial operational malfunctions. In this report, we bring the results of a field study performed in order to assess the impact of a decreased frequency of aircraft fuel tanks drainage regimes on the level of its fuel microbial contamination. The results implicate that the fuel tank draining regime and the ease of access to the draining points, both have significant impact on the level of the Jet fuel microbiological contamination. Furthermore, the results suggest that fuel tanks that are not drained as frequently as needed develop severe microbiological contamination, while fuel tanks which are drained weekly remain clean.

WAX DISPERSANT FOR TIGHT OILS

Nestor Soriano, Jennifer Sorrells, Jennifer Draper, Joe Stark

Historically, crude oils have been transported via pipeline within the U.S. However, the boom in shale oil production has largely occurred in areas not traditionally served by pipelines. The use of rail to move shale oils from production fields to refineries has therefore become more common, increasing approximately forty-fold since 2008. Shipping tight oil by railcar presents unique challenges. The paraffin content of these crudes can range from 10 – 20%, higher relative to more traditional oils.² Moreover, the paraffin chains are longer and less soluble in the hydrocarbon matrix. Tight oils therefore have a tendency to leave residue in rail cars and cause solids to build up on the walls of storage and transportation vessels. These residues result in decreased efficiency in the shipping operation and lead to increased costs related to downtime for cleaning of the vessel. Hence, the development of a wax dispersant to minimize paraffin deposition would be beneficial for shippers, terminals and refiners alike. This presentation will describe the use of a wax dispersant designed for the particular challenges of tight oils such as Eagle Ford and Bakken crudes. Data demonstrating efficacy in promoting wax dispersion in dispersion stability tests and preventing wax deposition in cold finger tests will be presented. It has been shown to improve pumpability and lower pour point. This additive can be used to improve profitability of shipping tight oils by rail, reduce downtime and costs associated with cleaning rail cars and improve the handling of these oils in storage at terminals and at refineries.

SESSION 11: FUEL CHEMISTRY, RESEARCH & DEVELOPMENT

CONSTRUCTION OF A REDUCED CHEMICAL KINETIC MECHANISM FOR PETROLEUM DIESEL AUTOXIDATION

Ehsan Alborzi, Simon G. Blakey, Theo Keane, and Anthony J. H. M. Meijer

Liquid Phase oxidation of neat petroleum diesel (EN590) was studied experimentally at different bulk temperatures using a near-isothermal plug flow reactor and a static small scale test device known as Petroxy. To simplify the complex reacting medium of diesel containing a large number of concurrent reactions and chemical species, a single component chemical, n-hexadecane was used for static thermal oxidative stability tests and product analysis. Theoretically, the automated reaction mechanism generator (RMG)1 was used to construct a detailed skeletal autoxidation scheme for hexadecane. Subsequently, the skeletal mechanism was reduced using a species lumping method. The resultant mechanism was optimized with a constrained minimization technique in order to calibrate the activation energies and pre exponential factors for the reduced mechanism. Furthermore, a series of tests were carried out using Petroxy in order to extend the reduced mechanism with the impact of antioxidant additive and reactive sulfurs on diesel autoxidation. Quantum chemistry and transition state theory were used to calculate the rate coefficients and activation energies for the interaction of these species with peroxy radicals or hydroperoxides. The proposed reduced mechanism is a promising basis for expansion with a surrogate fuel representative of biodiesel. This prospective mechanism can be used with computational fluid dynamics as a predictive tool for coke formation in diesel fuelled injection equipments.

REACTIVITY AND DEPOSITION PROPENSITY OF HYDROCARBONS UNDER SUPERCRITICAL PYROLYTIC REACTION CONDITIONS

Matthew J. DeWitt, Theodore Williams, Tyler Hendershott, Rich Striebich, Linda Shafer, Steven Zabarnick, Zachary West, Tim Edwards and Donald K. Phelps

There has been continued interest in the development and use of hydrocarbon-based fuels in advanced combustion and high-Mach propulsion systems and vehicles. Hydrocarbon fuels have many favorable characteristics for use in these applications, including relatively higher energy density and improved operational safety compared to cryogenic fuels. During operation, the fuel is required to provide cooling of the engine structure and subsystems due to high heat loads generated at higher Mach numbers. A portion of the heat sink can be provided via fuel sensible heating (e.g., $C_p\Delta T$), which can be supplemented by deliberate endothermic (e.g., heat-absorbing) reactions via thermal and/or catalytic cracking decomposition chemistry. Although the endothermic decomposition of the fuel can provide a significant amount of cooling capacity, an undesirable consequence is the formation of carbonaceous deposits (also known as coking) which can reduce fuel flow, increase resistance to heat transfer and foul injector nozzles. Improved understanding of the relationships between fuel chemical and physical properties on the corresponding reactivity and deposition characteristics is needed to provide the requisite basis for the development of advance high-speed aerospace platforms. Experimental and computational efforts are being performed using single components, model solvents and fully-

formulated jet and rocket fuels to improve the understanding of the correlations between fuel chemistry and reaction conditions on fuel performance. The experimental, analytical and computational methodologies employed and relevant findings will be presented.

EXPERIMENTAL STUDY OF THE IMPACT OF THE CHEMICAL COMPOSITION OF HEFA AND THE MOLECULAR STRUCTURE OF ADDED CYCLIC COMPOUNDS ON THE OXIDATIVE STRESS

Arij Ben Amara, Skander Kaoubi, Laurie Starck

Environmental and economic contexts has driven a handful of initiatives in the development of new sources and production processes for alternative aviation fuels. Several bioprocesses have emerged recently producing drop-in alternative jet fuels with different chemical compositions, which raises the interest of understanding the impact of the chemical composition on the oxidation kinetics of biojets, and their cooxidation with conventional fossil jet fuel or with aromatic compounds required for materials compatibility. The high complexity of the oxidation and cooxidation mechanisms (liquid phase kinetics, solvent effects) requires both experimental and theoretical works to assess the physical and chemical phenomena involved and to develop predictive tools. In this study, carried partly within CAER research program, the oxidation stability of two Hydrotreated Esters and Fatty acids (HEFA) jet fuels was measured with PetroOxy test device. The impact of the chemical composition (ratio of n-paraffins and iso-paraffins and chain length) on the induction period (IP) was assessed. The oxidation stability of selected pure aromatics and naphthenes and their blends with HEFA was measured. Results showed a significant impact of the molecular structure of aromatics and cyclic alkanes on HEFA Low temperature reactivity. Finally the oxidation stability of HEFA blends with conventional jet- A1 was measured from 293-323K. Results show a non-linear dependency of the IP with the volume fraction, illustrating a significant influence of the molecular structure of aromatics and cyclic alkanes on the oxidative stress of HEFA.

POSTER SESSION

TARGETING BACTERIAL ADAPTIVE MECHANISMS FOR PREVENTION OF FUEL BIODETERIORATION

Oscar N Ruiz, Richard C. Striebich, Thusitha S. Gunasekera

Microbial colonization of hydrocarbon fuels can affect fuel systems, vehicle performance and fuel quality. To develop effective prevention and mitigation approaches for fuel biofouling, better understanding of microbial adaptive mechanisms and their effects in fuel and fuel systems is needed. We have combined fuel degradation assays with genomics, transcriptomics and chemical analysis by GC-MS to characterize the metabolic response of bacteria and their unique hydrocarbon degradation profiles. Our results showed that upon exposure to fuel, bacteria activate multiple genes involved in hydrocarbon degradation, biofilm formation, iron and phosphorus acquisition, and toxic compound resistance (efflux pumps and porins). It was observed that n-alkanes are the preferred carbon source for many fuel degrading microbes but that aromatics and branched alkanes may be effectively degraded by specialized bacteria. During

bioreactor tests, bacteria mixed cultures were able to completely degrade many hydrocarbon components in fuel. Currently, we are using the acquired understanding of bacterial genetic and metabolism to develop detection and treatment methods to mitigate fuel biodeterioration.

CHARACTERISTICS IN A NEWLY DEVELOPED TURBINE ENGINE COMBUSTOR RESEARCH FACILITY AT AFRL

Edwin Corporan, Scott Stouffer, Matthew DeWitt, Tyler Hendershott, Chris Klingshirn

The effects of fuel aromatic concentration on combustion characteristics and emissions of a generic single nozzle swirl-stabilized combustor are discussed. The fuels tested include a conventional Jet A, a camelina-derived synthetic paraffinic kerosene (SPK), and the SPK doped with aromatics at 10 and 20% v/v concentrations. Experiments were performed at several equivalence ratios ($\Phi = 0.55$ to 0.70) and pressures up to four atmospheres. Combustion emissions were assessed via extractive measurements of particulate matter (PM) and gaseous species. The study was conducted in a recently built turbine engine combustor facility at the Air Force Research Laboratory (AFRL). It was designed to evaluate the performance and combustion characteristics of fuels with a wide range of physical and chemical properties, including fuels with properties outside the current fuel specification requirements. The facility is also configured to assess the operational performance of potential alternative fuels to efficiently reject unsuitable candidates prior to testing in larger combustors and engines. This will reduce the number of combustor tests required, which significantly reduces the cost of approving alternative aviation fuels. Test results show that PM emissions, both particle number (concentration) and mean particle size, increased with fuel aromatic content and combustor pressure. The largest relative increases in particle number and size between fuels with and without aromatics were observed at the lowest and highest equivalence ratios respectively. The importance of cycloparaffins concentration (and fuel hydrogen content) on soot formation was evident as Jet A fuel produced significantly higher soot emissions than the SPK + 20% aromatics despite containing nearly 80% lower concentration of soot-precursor naphthalenes. Regarding gaseous emissions, carbon monoxide (CO) emission indices were observed to increase exponentially as a function of equivalence ratio, following chemical equilibrium trends for all combustor pressures and fuels. Details of the facility design and capabilities, and additional results of combustor emissions as a function of fuels, pressure and equivalence ratio are discussed.

PRODUCTION OF AROMATIC DROP-IN JET FUEL FROM VEGETABLE OILS

Moshe Rabaev, Roxana Vidruk-Nehemya, Miron V. Landau, Moti Herskowitz

The catalytic conversion of vegetable oils to green drop-in jet fuel was carried out in mini-pilot trickle-bed reactor. The green drop-in jet fuel produced by our novel process met the specs (ASTM D7566, ASTM D1655) determined by a certified laboratory. Three hydrodeoxygenation routes were identified: (1) hydrodeoxygenation to water, (2) decarboxylation to CO₂ and (3) decarbonylation to CO. Hydrodeoxygenation and reforming of the triglycerides were performed on a proprietary, modified Pt-SAPO-11/ γ -Al₂O₃ catalyst in a trickle-bed reactor to produce hydrocarbons with content of 14-16% monoaromatic and >50% isoparaffinic compounds. This

stage was followed by fractionation, mild hydrocracking on Ni₂P/HY catalyst and additional isomerization on Pt-SAPO-11/ γ -Al₂O₃, to achieve after fractionation >50 wt% of jet fuel with >8% aromatics. Stable operation of the catalytic process was recorded for >1000h on stream, running the hydrodeoxygenation at 375-380°C, 30 atm and LHSV = 1h⁻¹. The hydrocracking and additional isomerization at 300-330°C and 350°C, respectively, 30 atm and LHSV = 1-3h⁻¹. The light and heavy fraction recovered can be further processed to yield gasoline and diesel products.

CHARACTERIZATION OF WATER SOLUBLE DEPOSITS IN AIRCRAFT FUEL SYSTEMS

E. Bowman, N. Weir, S. Samuel, D. Bowman, P. Glaser, E. Telfeyan, R. Davis, N. McLean, I. Kosilkin, JP. Belières

Over the past few years, several airlines have been subject to disruptive incidents in North America, involving two airframe OEMs and several engine OEMs. As a result, a large investigation was launched, and a root cause analysis determined that fuel contamination was the likely cause. Part of the investigation focused on the evaluation of jet fuel quality and fuel handling equipment and procedures. We will briefly describe the characterization of these incidents at the airplane level and summarize the findings of this investigation. One of the most interesting findings was the discovery of water soluble deposits in engine hardware that do not appear to be related to byproducts of fuel thermal oxidation, a phenomenon commonly referred to as fuel lacquering (water insoluble). Although chemical characterization of the water soluble deposits has been performed, the source and mechanism of deposition remain unknown. Analysis of microbial contamination in aircraft wing tank fuel and water was also done in an effort to better understand its extent and relation to the observed deposits.

A NEW YEAST ISOLATED FROM AVIATION KEROSENE

Joan Kelley, Alan G Buddie, Paul D Bridge, and Matthew J Ryan

During an extensive survey of microbial contamination in aviation fuels, a previously unrecorded yeast was isolated from more than one sample. This novel yeast proved to be a new species of *Candida*. Ribosomal RNA gene sequence analysis of internal transcribed spacer (ITS) regions (including 5.8S subunit) plus the 26S D/1D/2 domains showed the strain to cluster within the *Candida membranifaciens* clade nearest to, but distinct from, *Candida tumulicola*. Physiological and biochemical tests supported the position as a separate taxon. Two strains (IMI 395605 and IMI 395606) of this novel yeast named *Candida keroseneae* sp. nov., were isolated, characterised and described. The yeast was assessed for its effect on the main constituent hydrocarbons of aviation fuel. GC analysis suggested that *C. keroseneae* was only able to utilise a narrow range of alkanes. While growth occurred readily on the fuel it was slower growing than other more common yeast isolates and is probably out competed in many situations.

SYNTHETIC PHENOLIC ANTIOXIDANTS IN MIDDLE DISTILLATE FUELS ANALYSED BY GAS CHROMATOGRAPHY WITH TRIPLE QUADRUPOLE MASS SPECTROMETRY.

Renée L. Webster, Paul M. Rawson, David J. Evans, Philip J. Marriott

The inclusion of synthetic phenolic antioxidants (SPA) in hydroprocessed middle distillate fuels is mandated in jet fuel specifications at a maximum total concentration of 24 mg/L. Currently it is not possible to analytically confirm the SPA concentration once SPA are added to fuel, given the many possible compounds which may be present in the antioxidant package, and the complexity of the base fuel which leads to considerable matrix interference. Methods that provide the ability to positively identify and quantify specific SPAs present in any given fuel is desirable, particularly when fuels experience stability problems and/or become contaminated and where these may be treated by addition of synthetic antioxidants. A method for the selective determination and quantification of 10 synthetic phenolic antioxidants (SPA) in jet and diesel fuels has been developed. The analytical procedure involves no sample preparation, and uses direct injection of the diluted parent fuel into the GC column. Gas chromatography with triple quadrupole mass spectrometry was used to quantify synthetic phenolic antioxidants in the range of 0.1-20 mg/L. Precision was in the range of 3-9%. The method is demonstrated to be rugged and robust, and since no extraction is required, does not require estimation of extraction efficiencies. It is generally suited to volatile SPA compounds included in jet and diesel fuel specifications. Here, we present a new method of GC coupled to the MS/MS instrumentation appropriate for the estimation of SPA in fresh and in-service middle distillate fuels stored on military bases, tankers or in use on aviation or naval platforms.

EFFECTS OF BIODIESEL CONTAMINATION ON OXIDATIVE AND STORAGE STABILITY OF NEAT AND BLENDED HYDROPROCESSED RENEWABLE DIESEL

Jinxia Fu and Scott Q. Turn

The development and utilization of alternative fuels is an ambitious global energy goal owing to depletion of fossil fuel sources, increases in global population and forecasted, long-term oil price, and concerns about global warming. Although hydroprocessing vegetable oils and animal fats has advantages over transesterification technology of 1st generation fatty-acid methyl ester biodiesel, both first- and second-generation renewable fuels are employed by the US Navy. Hydroprocessed renewable diesel (HRD-76) has been demonstrated as a compatible blend stock with marine diesel (F-76) by the US Navy, while the usage of biodiesel blends are allowed only for on-shore operation. Concern has been raised about the potential biodiesel contamination of F-76, HRD-76, and their blends from the use of common fuel handling systems both at home, and in foreign ports where biodiesel use is more pervasive. The present study investigates the influence of biodiesel contamination on physicochemical properties and stabilities of F-76, HRD-76, and their blends. Physical properties and chemical composition of F-76, HRD-76, and biodiesel were measured. Long-term (ASTM D4625) and accelerated (ASTM D5304) test methods were applied to investigate the influence of biodiesel on storage stability and fuel properties, such as viscosity, density, heating value, peroxide value etc. after long-term storage of HRD-76, F-76, and their blends. In addition, ASTM D2274 tests were conducted to study the effect of biodiesel contamination on oxidation stability and thermochemical properties of neat

and blended fuels. Extended ASTM D2274 tests were also conducted to investigate the influence of long-term oxidation on fuel properties.

EDXRF METHOD FOR ULTRALOW LEVEL SULFUR IN GASOLINE ANALYSIS TO COMPLY WITH U.S. EPA TIER 3 RULING

Allen Bickel

US EPA's Tier 3 Ruling reduces allowed sulfur concentrations in gasoline from an average of 30 mg/kg to an average of 10 mg/kg, beginning in 2017. Refiners, importers and biofuel blenders of gasoline will be required to perform sulfur analysis at these ultra-low levels to report compliance throughout the supply chain. The Ruling also enacted use of a PBMS (Performance Based Measurement System) approach to allow reporting laboratories new flexibility regarding the sulfur test method they may use. Use of consensus group (e.g. ASTM) standardized test methods and mandatory quality control practices validate adequate measurement quality. The objective of this project is to demonstrate that the recently revised ASTM D7220 sulfur test method initially used for EPA's 2006 Diesel Ruling which reduced allowed sulfur concentration down to 15 PPM, can also be utilized to meet EPA's Tier 3 Ruling. D7220 takes advantage of monochromatic EDXRF to reduce background radiation interference and produce a single energy of excitation for sulfur. Experiments were conducted using a monochromatic EDXRF system with a close-coupled, doubly curved HOPG crystal to reflect Ag K α radiation, a vacuum chamber, a Pelletier-cooled Ag anode X-ray tube, and a Silicon Drift Detector. Sample volumes of 5 mL were analyzed. Testing parameters and example data that exhibit pass/fail conditions are described. Findings conclude that compliance with all EPA PBMS requirements for both ultra-low sulfur diesel and gasoline for sulfur levels at and below 3 mg/kg, well within the Tier 3 Ruling, is demonstrated using the recently revised ASTM D7220 Method.

FIELD ANALYSIS OF FUEL USING A PORTABLE NEAR-INFRARED SPECTROMETER

Carl Brouillette, Wayne Smith, Chetan Shende, and Stuart Farquharson

Fuel quality is becoming increasingly important in many countries where fuel theft occurs in the form of diluting shipments with less expensive petroleum products. Diluted fuels with inferior chemical and physical properties lead to decreased engine performance and ultimately engine failure. These properties include aromatic, fuel system icing inhibitor, olefinic, naphthene, oxygenate, and saturate content; cetane and octane numbers; cloud, distillation, flash, freezing, and pour points; density (API gravity), Reid vapor pressure, and viscosity. Complete analysis of a suspect fuel requires multiple analyzers, typically one per property, and as much as 8 hours. Such analysis is not always performed. Consequently, there exists a need to rapidly verify fuel quality upon receipt. Often, such verification must be performed far from a lab containing standard fuel analysis instruments and apparatus. To satisfy this need, we have developed an inexpensive, compact (4x7x8", 6 lb) fuel analyzer based on near-infrared spectroscopy that employs chemometrics to determine the 16 properties listed above in 10 seconds, using only 3 mL of sample. This presentation describes the analyzer and the chemometric analysis.

REDUCED EMISSIONS VIA SYNTHETIC AROMATIC KEROSENE

Cynthia Ginestra, Joanna Bauldreay, Greg Hemighaus, Brice Dally, Pervez Canteenwalla, and Prem Lobo

The various composition profiles of emerging synthetic jet fuels have the potential to create jet fuels that are fit-for-purpose and also minimize environmental impact due to reduced exhaust emissions. We present data aimed to explore the links between jet fuel composition and gaseous and particulate matter emissions. Smoke point trends as a function of fuel aromatics levels were examined for various jet fuel samples, including conventional, semi-synthetic, and fully-synthetic blends. Bio-derived synthetic aromatics were provided by Virent's Synthetic Aromatic Kerosene. Subsequently, conventional and synthetic-containing jet fuels with matching total aromatic contents were combusted in a small turbojet engine at simulated altitude conditions. The resulting emissions profiles were measured and compared.

DETECTION AND ANALYSIS OF HIGH MOLECULAR WEIGHT CONTAMINANTS IN FUELS BY ULTRA HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Thomas N. Loegel Kristina M. Myers, Iwona A. Leska and Robert E. Morris

Laboratory protocols have been developed to detect, and in some cases quantify, polar and non-polar contaminants in fuels, such as light cycle oils, heavy diesel fractions in jet fuel, etc. All of these methods are based on separation and concentration of the polar contaminants by either a liquid-liquid or liquid-solid extraction scheme. Maximum operating temperatures of GC capillary column stationary phases limit detection of heavy contaminants to a maximum of approximately C30 (m.w. ~ 400-450), even though that range can be extended to around C50 (m.w. ~ 702) with high-temperature metal columns. In addition, many of these larger molecules do not readily elute from GC columns and at temperatures greater than approximately 350°C, where pyrolysis becomes more likely. An ultrahigh high performance liquid chromatography (UHPLC) UV-vis method was developed to determine the presence and quantify the amount of polar light cycle oil (LCO) by detection of heavy aromatic constituents. This method is suitable for F-76 and ULSD petroleum based diesel fuels with suspected LCO contamination greater than 1% by volume. The sample extraction procedure and HPLC separation can also be used to determine if a jet fuel has been comingled with diesel fuel. A high temperature GC-MS method was also developed to characterize the compositions of heavy contaminants in jet and diesel fuels. To detect high molecular weight non-polar contaminants, a high-temperature UHPLC method was developed, based on method used to characterize large alkanes in high density polyethylene. Using an external column oven to achieve temperatures between 90 °C and 100 °C on a porous graphite stationary phase, it is possible to achieve separation of large alkanes (C40-C110). An evaporative light scattering detector was used with selected n-alkane standards to estimate the amount of large, non-polar materials present in the fuel.

A TRANSIENT MODEL FOR SURFACE DEPOSIT GROWTH IN GT BURNER FEED ARM WITH CONTRACTION / EXPANSION GEOMETRY FEATURES

Ehsan Alborzi and Simon G.Blakey

A novel, fuel specific, wall reaction model for deposition stage of aviation fuel thermal oxidative stability has been proposed and implemented into computational fluid dynamics (CFD) commercial code. The model has been successfully validated against the surface deposition data generated in a replicated feed arm burner with cylindrical geometry. The model agrees within 8% of the total carbon burn off measured data and within an average of 28% of the transient indirect deposit measurements. Subsequently, the validated model was used with CFD for comparison against experimental data corresponding to another replicated feed arm with contraction/expansion geometry. The model agrees within 25% of the total carbon burn off measured data and within an average of 21% of the indirect deposit thickness measurement. The CFD analysis for the latter case provided visualization of the recirculation zone of the expansion and contraction and their impact on flow field as expected and the evidence of effect these zones had on the heat transfer between tube wall and bulk fuel. The thorough definition of the thermal boundary conditions at the fuel wetted surface has been shown to be critical to the prediction of deposit formation.

HOW WILL NOVEL FUELS AND MATERIAL IMPACT MICROBIAL CONTAMINATION IN AIRCRAFT FUEL SYSTEMS?

Alexander McFarlane, Dr. Steve Thornton, and Dr. Stephen Rolfe

It is well established that jet fuel systems are susceptible to microbial attack, as they provide all of the chemical and physiological requirements for biological growth. The introduction of alternative fuels and materials into the supply chain is likely to impact microbial community structure and function with the potential for new risks. This project explores the impact of alternative fuels and novel composite materials on microbial community structure, biofilm development and function with the aim of identifying the underlying biological, chemical and physical processes. Our work has focused on a) characterising the microbial communities present in conventional aircraft fuel systems and their role in biofilm development, biocorrosion and fuel degradation, and b) the effect of introducing alternative fuels and new material formulations on these processes. We have used molecular genetic techniques to characterise the microbial communities found in diverse conventional fuel systems and used these data to design multifactorial laboratory microcosm experiments in which parameters such as microbial community structure, fuel type and surface composition were varied. Our data shows that alternative fuels and materials strongly influence microbial growth rate, community structure and cell attachment. This project will help further the understanding of the principles that govern biofilm formation in aircraft fuel systems and the impact of introducing alternative fuels and materials into the supply chain.