15^{TH} INTERNATIONAL SYMPOSIUM ON STABILITY, HANDLING AND USE OF LIQUID FUELS
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Abstract Summaries

Keynote Address:

HOW EUROPEAN STANDARDS GUARANTEE FUEL QUALITY, VEHICLE FUNCTIONING AND EMISSIONS

Ortwin Costenoble, M.Sc.

Guaranteeing fuel quality in Europe and selling the product to customers, is not standard. Even though the European Standardization Committee (CEN) develops fuel specification and test method standards which become the national standard in 37 European countries. The fact that Directives align the legal requirements regarding emissions of vehicles, the biofuel blends allowed on the market and the alternative fuel infrastructure and marking across Europe, several peculiarities remain.

Chevron Award of Excellence in Honor of John Bacha:

PHENOLS AND AROMATIC METHYL ETHERS FROM BIOMASS PYROLYSIS OIL: IMPLICATIONS FOR JET FUEL STABILITY

Mariam Ajam, Carl L Viljoen, Chris Woolard, and Eric van Steen

Jet fuel is used as a heat sink for aircraft systems and is required to be thermally stable. Jet fuel instability could cause deposits, which may foul aircraft components. Renewable jet fuel may be produced from biomass pyrolysis oil, although concerns may exist about its high phenolic content, since some phenols have a high propensity to form deposits. This study has successfully demonstrated three options for improving the thermal stability of renewable jet fuel derived from biomass pyrolysis oil, viz. severe hydrotreatment, solid-phase extraction (i.e. passing the jet fuel over a silica column to remove polar hetero-atomic species) and etherification of the phenols to aromatic methyl ethers. A two-stage, severe hydrotreatment of biomass pyrolysis oil produced kerosene samples with a very low oxygen content (<0.5 wt%). These kerosenes showed low depositing characteristics (0.78-1.52 μg/cm2) when measured using a quartz crystal microbalance (QCM). Severe hydrotreatment of biomass pyrolysis oil is recommended to produce renewable jet fuel via this route to meet the current stringent jet fuel specifications. The severe conditions that are required, however, make such a process economically impractical. A less severe hydrotreatment, followed by silica treatment or by the etherification of any phenols present in the jet fuel to methyl ethers, were shown to produce a thermally stable jet fuel. The conversion of trace levels of phenols to aromatic methyl ethers was evaluated in this study as a novel method of improving jet fuel thermal stability. Mixtures of phenols, likely present in petroleum and biomass pyrolysis oil-derived jet fuels, were etherified by conversion to phenolate ions using NaOH or NaH, followed by methylation with dimethyl sulphate. Most phenols effectively etherified, except hindered phenols with alkyl groups at the 2 and 6 positions. The thermal and oxidative stability of two model fuels and two real fuels derived from biomass pyrolysis oil, containing a variety of phenols and/or aromatic methyl ethers, were studied using a QCM. Fuels containing phenols displayed high deposition propensities whereas fuels containing the corresponding aromatic methyl ethers displayed much reduced deposition propensities. The conversion of trace phenols in renewable jet fuel derived from biomass pyrolysis oil to methyl ethers significantly improved the thermal stability of the fuel. This study is the first to evaluate the effect of aromatic methyl ethers on jet fuel properties which were then compared to fuels containing the corresponding phenols. Phenols were detrimental to freezing point, acid number and thermal stability while aromatic methyl ethers had no negative impact. Silica treatment of the renewable jet fuel derived from biomass pyrolysis oil also reduced its deposition propensity, due to the removal of polar hetero-atomic species such as phenols.

SESSION 1: FUEL PRODUCTION AND QUALITY CONTROL

STABILITY CHARACTERIZATION OF RESID HYDROCRACKING EFFLUENTS BY THE S-VALUE METHOD (ASTM D7157): EFFECT OF THE ANALYTICAL PARAMETERS

Jérémie Barbier, André Diot, Matthieu Drellard, João Marques

Ebullated-bed resid hydrocracking (RHC) process is used to upgrade vacuum residues feedstock. This is a catalytic process that allows to convert heavy oils into gasoline and gasoil and to remove contaminants such as sulphur and metals from heavy feeds. By 2020 the sulphur content of marine fuel oils should not exceed 0.5% has decided by the International Maritime Organization in order to significantly reduce sulphur emissions from ships. RHC process may contribute to the production of low sulfur marine fuels. The stability of RHC heavy effluents must be controlled in order to limit sediments and sediments precursors formation. Therefore, the S-value method (ASTM D7157) was developed to quantify the intrinsic stability of asphaltenes in residual products from thermal and hydrocracking processes. This method consists on a titration using a solvent/antisolvent couple (toluene/n-heptane) and an optical detection of the asphaltenes precipitation. 3 parameters are derived: S parameter which is representative of the intrinsic stability of oil, Sa parameter that quantifies the peptizability of asphaltenes and S0 that represents the peptizing power of oil. The objective of this study is to investigate the relevance of the S-Value method to characterize the stability of RHC effluents. Different RHC pilot plant effluents, obtained from an Ural straight run vacuum residue treated under different operating conditions of residence times and temperatures, were used in this study. Results show that for RHC effluents with weak intrinsic stability, the S-value parameters have poor repeatability and the confidence intervals of parameters are significantly larger than the ones described in the standard method. Therefore, two parameters of S-value method were studied: the anti-solvent addition rate flow and the polarity differential of solvent/anti-solvent couple. Results show that the kinetics of asphaltenes precipitation is a key phenomenon, and titration conditions must be adapted in order to improve the characterization of high conversion RHC effluents. A new software was developed allowing to adapt these conditions.

FACTORS AFFECTING FILTERABILITY OF MIDDLE DISTILLATE FUELS

David A. Daniels, Andrew McKnight, Arthur Fogiel, Alex Belly, Christopher LeMieux

Modern diesel engines continue to evolve to meet ever more stringent emissions standards. This evolution includes fuel injection equipment (FIE) design features that are increasingly sensitive to fuel-borne contaminants. Subsequently engine performance and durability are linked to fuel cleanliness. The industry has turned to ultrafine filtration, both on-board the vehicle as well as in the upstream diesel distribution system, in order to meet today's cleanliness challenges. The introduction of ultrafine filtration has generated a new set of concerns and problems for the industry as a whole. This paper is the first in a series that highlights important differences between various high efficiency bulk filtration media. The differences could pose serious operational problems and expense to the end user. A climate-controlled filtration rig was used to evaluate the flow rate through various filter media under real world temperature condition. The filtration rig clearly demonstrated dramatic flow rate variation with different bulk fuel filters of similar porosity and efficiency. This paper further highlights that different filter have disparate sensitivity to fuel temperature, fuel properties, heritage additives, porosity, and filter media.

A THEORETICAL AND FULL SCALE INVESTIGATION INTO THE USE OF TANK SETTLING TO REMOVE WATER AND SOLID CONTAMINANTS FROM AVIATION FUEL

Steve D Anderson, Alisdair Q Clark, Andrew Glendinning, Gary Norris

Aviation represents a unique and important part of the global transport infrastructure with more than 100,000 flights each day linking countries and continents across the world carrying 3.3 billion passengers per annum[1]. To achieve this goal the Aviation Industry have developed technically advanced engines and aircraft with stringent specifications for fuel quality[2]. In this paper a detailed study of fuel cleanliness is undertaken with focus on tank settling time to remove trace contaminants. Traditionally tank settling has been seen as a primary route to eliminate particulate and water matter with guidelines of 3 hours per meter tank height[3]. A theoretical and full scale investigation challenges the validity of this approach in light of soluble/free water equilibrium, common contaminants and use of modern filtration equipment. As part of the study a typical aviation terminal tank of 60 feet height is examined over 48 hours on receipt of a cargo which has experienced a 20 °C temperature change since load-port. Analytical techniques include Karl-Fischer, particle counting/co- solvent, scanning electron microscopy to determine the true value of tank settling/floating suction on fuel cleanliness.

SESSION 2: MARINE DIESEL FUELS

EFFECTS OF AROMATIC TYPE AND CONCENTRATION ON PROPERTIES AND STABILITY OF ALTERNATIVE MARINE DIESEL

Jinxia Fu1, Scott Q. Turn

The use of biofuels has been a part of the U.S. Navy's approach to deploy the "Great Green Fleet". Hydroprocessed renewable diesel (HRD-76), and direct sugar to hydrocarbon (DSH-76), also known as synthesized isoparaffin (SIP-76), have been produced in sufficient quantity for testing by the US Navy, and demonstrated as compatible replacements or blend stock with marine diesel (NATO F-76). Operational limitations with respect to the lubricity, seal swell and cold-flow properties, however, need to be improved before using 100% HRD-76 or SIP-76. Aromatics are known to improve seal swell and low-temperature characteristics, and a minimum of 8 wt% aromatics is required in marine diesel or diesel blends. In this study, three commercial aromatic blends and 15 pure alkyl aromatics which are present in petroleum diesel were added (individually and as a blend) to HRD-76 and SIP-76 at various concentrations to investigate their influence on material compatibility, storage and oxidation stability, physicochemical properties, and low- temperature qualities. Both experimental and computational methods were used to study the propensity of different aromatic species to enhance qualities of HRD-76 and SIP-76. In addition, the impacts of aromatic additives on biofuel water content and vapor pressure were also investigated.

THE IMPACT OF CHANGING REGULATIONS ON MARINE FUEL QUALITY AND THE ROLE AND EFFECTIVENESS OF FUEL ADDITIVES

Simon Mulqueen, Michael Banning

In the late 1980's the International Maritime Organisation (IMO) started work on reducing air pollution from ships. Since then in a parallel movement to automotive application, the introduction of further legislation and emission regulations have seen the introduction of low sulphur fuels. Further controls have also been implemented with the introduction of emissions control areas (ECA) in coastal waters and ships trading in designated emission control areas now have to use on board fuel oil with a sulphur content of no more than 0.10% from 1 January 2015, against a limit of 1.00% sulphur in effect up until 31 December 2014. As a consequence from 2015 there has been a change in the middle distillate versus residual fuel demand, directly as a result of the ECA legislation. The higher middle distillate fuel consumption has inevitably suppressed residual fuel quality, and therefore value. Subsequently refiners are looking to adopt deeper conversion processes to meet the extra demand of the market, resulting in a further deterioration of the ignition, combustion and stability properties of the provided residual fuel. The 2015 ECA legislation further challenges fuel stability since future fuel changeover will be between middle distillate and residual fuels, and at a slower change over rate, maximizing the incompatibility risk. Middle distillate fuel can also represent its own risks, since increased consumption requires additional storage space onboard, along with longer storage periods. This means risks of inadequate lubricity, stability and cold flow properties must be considered.

The market has also seen the emergence of several hybrid “ECA Compliant” fuels, which themselves present specific challenges. In all of the above fuel additives can play a key role in mitigating many of the quality and operability concerns. This paper discusses and demonstrates how fuel additives are a reliable and cost effective solution focused directly on solving fuel quality issues, along with the potential operational challenges. The introduction of new legislation has marked a step change in the grades of bunker fuels available and in service. As a result a step change in fuel quality has occurred, which may act to further exacerbate existing challenges. Challenges associated with residual and distillate fuels will be examined, plus those associated with changeover between the two. A summary of new ECA Compliant fuels, their properties, and their advantages and disadvantages versus conventional fuels will also be considered.

SESSION 3: FUEL CONTAMINATION

IMPACT OF WATER BOTTOMS ON AVIATION TURBINE FUEL CHLORIDE CONTENT

Paul P. Wells

Elevated chloride levels in aviation turbine fuel can cause corrosive and abrasive wear of aircraft fuel control systems. Chloride contamination is most likely the result of carryover from a refinery salt dryer or seawater contamination during marine transport. A series of high profile incidents were caused by chloride contamination in 1974. In the most serious incident, two of four Boeing 747 main engines were shutdown in flight. Analysis revealed that aircraft fuel tank water sumps contained 11,900 to 21,900 ppm sodium chloride. An ensuing report by the International Air Transport Association (IATA) noted that there were no detrimental effects on aircraft hardware when water sumps contained up to 500 ppm sodium chloride. Issued in April 1990 (but since withdrawn), the Australian Defence Standard 5240B for aviation turbine fuel contained a requirement for ≤0.15 mg/L sodium chloride. With the passage of time, it is unknown why this concentration was selected or if there is any relationship to the IATA guidance above. ASTM D7959, a standard test method to measure chloride levels in aviation turbine fuel has been developed and a reference to the methodology has been added to the D1655 appendix. The details of the test will be reviewed. The impact of water bottoms on aviation turbine fuel chloride content via D7959 will be investigated. The key variables investigated will be chloride content of the water bottoms and additive content of the fuel. The ability of current D1655 requirements for water separation and conductivity to function as a substitute control of fuel chloride content will also be investigated.

APPLICATION OF MATRIX-ASSISTED LASER DESORPTION/IONIZATION MASS SPECTROMETRY TO THE CHARACTERIZATION OF HIGH MOLECULAR WEIGHT FUEL CONTAMINANTS

Thomas N. Loegel, Jeffrey A. Cramer, and Iwona A. Leska

During even routine fuel handling operations, it is possible to introduce high molecular weight (HMW) contaminants, such as lubricants and greases, to fuels, thus contaminating them and negatively impacting their stability and performance. To address this fuel handling challenge, analytical methodologies based on high-performance liquid chromatography combined with an evaporative light scattering detector (HPLC-ELSD) have previously been developed in our laboratory to detect and quantify HMW contaminants in fuels. However, both the high molecular masses that are required to pass through the HPLC columns and the relatively limited selectivity of the ELSD data can interfere with attempts to identify the sources of HMW contamination using HPLC-ELSD methodologies. This presentation will cover the use of matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, combined with a sampling technique adapted from the forensics literature, to characterize the high molecular masses collected from contaminated fuel samples more thoroughly.

QUANTIFICATION OF PHOSPHATE ESTER-BASED HYDRAULIC FLUID IN JET FUEL

Diana Gertopski Stamker, Moshe Rabaev, Konstantin Tartakovsky

Phosphate ester-based hydraulic fluids are commonly used in aviation, among others due to their fire resistance properties. However, they also cause corrosion of metals and swelling of elastomer and polymer seals. Contamination of jet fuel with hydraulic fluid may cause serious engine failure, and due to the corrosive effect of phosphate esters on cobalt, the level of phosphate ester must not exceed 1 ppm in jet fuel. The jet fuel should be tested for traces of phosphate compounds. This article describes methods for identification and quantification of Exxon and Skydrol hydraulic fluid contamination in jet fuel. Both of the fluids are composed of tri-butyl phosphate. Jet fuel chromatogram peaks interfere with identifying this compound's main peak, thus two techniques to separate the jet fuel peaks from the tri-butyl phosphate peaks were developed. One is based on a solid phase extraction procedure followed by identification and quantification which is carried out using a gas chromatograph equipped with a mass spectrometer or by a gas chromatograph equipped with a flame ionization detector. The other separation technique is single-staged, where the separation and analysis are carried out by a gas chromatograph equipped with a DB-WAX column and MS. Lowest level of detection reached was 0.1 ppm of tri-butyl phosphate in jet fuel; approximately 10 times lower than the limit. Linearity was achieved in all analysis methods up to contamination of 100 ppm.

COLD FILTER BLOCKING TENDENCY AS A PREDICTOR FOR LOW TEMPERATURE OPERABILITY OF DIESEL FUELS

Ian. P. Mylrea, Jerry Burton, David Swan

A new Energy Institute test method, IP 618 (Cold Filter Blocking Tendency) has been developed in response to diesel fuel filterability issues during winter months. Over several winters the number of diesel vehicle breakdowns due to blocked fuel filters is considerably above the norm, when compared to the warmer months. As was stated in the introductory remarks at the June 2015 CEN/TC19/WG24 Filter Blocking Workshop, in London, "a wide range of vehicles is being affected in several European countries, and there is a possible causal link with base fuel quality, FAME composition, cold flow additives and oxidation stability affects"[4]. It is considered by many experts to be a complex issue, not only related to the fuel, but also the design of the vehicle filtration systems. A clear correlation has been demonstrated between cold days in the UK and the number of vehicle breakdowns, with overnight minimum temperatures below 3 oC causing a significant rise. Due to the complexity of the issue, the experts were motivated to develop a laboratory scale performance test, to help identify those fuels likely to cause field issues. Following extensive industry participation, IP 618 was published with full precision in November 2016 and was used during the winter 2016/17 to gain experience on field fuels. This paper describes the background and development of the test method, the work to-date and available data.

A USER'S PERSPECTIVE AND EXPERIENCE WITH PARTICLE COUNTING IN LIQUID FUELS – UNITED STATES ARMY

Joel A. Schmitigal

Following several years of research within the Department of Defense, limits for light obscuration particle counting were published in MIL-DTL-83133J in December of 2015 followed by inclusion in MIL-STD-3004D change 1 in March 2016. Over 2500 field samples have been analyzed by both particle counter technologies and gravimetric analysis for comparison purposes, yielding a 92% go/no-go agreement between the established 19/17/14/13 ISO code limits and 1.0 mg/L gravimetric contamination limit.

SESSION 4: BIODIESEL AND DIESEL

STORAGE STABILITY STUDIES AND SHELF LIFE DETERMINATIONS OF COMMERCIAL BRAZILIAN BIODIESELS STOCKED IN SUBTROPICAL CONDITIONS IN CARBON STEEL CONTAINERS

Eduardo H. de S. Cavalcanti, Adriane Zimmer, Marcos Ferrão, Fatima Menezes Bento

The storage stability of biodiesel is a matter of great concern notably in continental countries that possess complex distribution and retail fuels chains. This is particularly true in Brazil also due to the long distances from the production biodiesel regions to the refineries where it is added to the diesel. On top of that there are at least six biomes in Brazil ranging from cold high land regions in the South up to hot wet tropical and semi- arid climates in the in the North and Northeast, respectively. Subtropical weather however prevails is most of the economically active and urban regions of the country where most diesel consumers are located. This diversity added to the fact that most of the biodiesel plants are concentrated in the Midwest and Southern parts of the country poises an extra logistic challenge to keep the quality under full control all over the distribution, commercialization and retail chains. The biodiesel should be 100% in line with the specifications, so that total quality should be guaranteed up to the moment of fuel ignition in the diesel engines. At present almost 85% of the Brazilian Biodiesel is made of soya oil. It is well known the high susceptibility to oxidation of soya derived biodiesel products. This sort of aging is aggravated in tropical humid countries due to the high hygroscopic nature of biodiesel. As a result the tendency of biodiesel to suffer significant changes over atmospheric storage time is always a matter of concern, as physical and chemical keys properties tend to go out of specification with serious risks to the end users of diesel-biodiesel fuel, particularly for pumps, parts, tanks and injection systems components of vehicle and industrial engines employed in urban, off-road and in-land applications. In the present work we have studied the long term storage stability of three different commercial Brazilian methyl esters made from pure soy oil (SoYB100) containing TBHQ commercial antioxidant, 65% soybean 35% beef tallow (SoyBTBlend6535) and pure beef tallow (BTB100pure). They initially remained stored in HDPE 60 L containers sent completely full by the biodiesel producers and kept stored at the laboratory premises for 60 days. This preliminary period was meant as most of commercial biodiesel stay in average 60 days stored or travelling before being pumped to the diesel, notably at far end regions of the country. Subsequently 1L carbon steel canisters with a small top hole giving access to the atmosphere were 80% filled with these biodiesels and kept stored for 90 days under sheltered but exposed to air, local heat and humidity conditions. Temperature (T) and relative humidity (UR%) at the open corridor of the laboratory - where the carbon steel canisters were left aside, were on-line monitored during the 90 days testing period. Monthly analyses of aspect, water content, specific gravity, kinematic viscosity, acid number and oxidation stability of the stored biodiesels were also conducted.

THERMAL AND OXIDATIVE INSTABILITY IN BIODIESEL BLENDS DURING VEHICLE USE AND ONBOARD FUEL STORAGE

Steven R. Westbrook

This paper covers the results of Coordinating Research Council (CRC) Project AVFL-17c to study the thermal and oxidative stability of biodiesel blends during vehicle use and onboard storage. The CRC considers the work reported herein as Phase I of a potentially larger-scope project. The objective of this first phase was to examine the impacts of various aspects of fuel stability (temperature, pressure, oxidation, free radical formation, acid formation, etc.) on biodiesel blends during onboard vehicle use and storage conditions. The project was divided into 6 different tasks: 1) conduct a literature review of oxidation and thermal fuel stability parameters as pertains to vehicle use and storage, 2) make selections of pertinent vehicle technology pertaining to possible stability parameters, 3) identify and obtain test fuels, 4) vehicle testing to collect fuel system condition data and effects on biodiesel degradation, 5) develop bench-scale, fuel-stressing methodology to mimic the conditions that fuel experiences in HPCR fuel systems, and 6) provide recommendations for Phase II (fuel effects testing) to CRC. Biodiesel blends (B0, B5, and B20) were tested in vehicles using on-road and dynamometer testing. Fuel samples were collected from vehicle fuel tanks during test cycles and analyzed using tests selected to indicate changes in thermal and oxidative stability. Test fuels were also stressed using a bench-scale fuel stressing apparatus. Samples of the stressed fuel, taken at pre-selected intervals, were also tested using the same protocol as the vehicle fuel tank samples. Test results from all samples were analyzed for correlations between bench-scale and vehicle stressing.

DEMYSTIFYING THE ROLE OF DIESEL FUEL COMPOSITION IN INTERNAL INJECTOR DEPOSITS WITH VASE

David J Abdallah, Scott K Berkhous, Krystal B Wrigley, Matt I Watkins, Paul Lacey

Diesel fuel’s thermal stability is becoming a critical property as high pressure common rail fuel systems continue to intensify the extreme temperature environments encountered by the fuel prior to combustion. If the temperature exceeds the fuel’s thermal oxidative stability breakpoint it can lead to deposit formation on the hot internal injector surfaces causing reduced heat exchange efficiency, fuel flow constrictions, and sticking of close fitting parts. Owing to the important role deposit thickness on fuel-wetted hot metal surfaces plays in injector durability performance, precise quantitative measurement are of great importance. Here we report the use of Variable Angle Spectroscopic Ellipsometer (VASE) to afford precise deposit thickness and profile measurements on injector parts which provides many benefits over deposit color visual evaluations used in the past. A series of rig tests were conducted using commercially available fuel injectors with diesel fuels of varying composition. The fuel deposit thickness profile and optical characterization on the injector parts is used to clarify the role of fuel components in producing internal injector deposits. In the limited set of fuels investigated the results revealed that conventional diesel fuels blended with FAME based biodiesels had relatively more deposits than the fuel without. Moreover, biodiesel blends containing cetane improver additive had relatively more deposit than the fuel without. Mapping of deposit thicknesses across the surface revealed thicker deposits toward the injector needles tip highlighting a greater level of heat soaking of the fuel as it travels toward the hotter injector fuel outlet. In some of the tests that used fuels containing biodiesels the deposits on internal injector parts were found to be more translucent than the deposits produced with the same base fuel without biodiesel illustrating that bulk fuel composition differences lead to bulk deposit composition differences. Plots of the imaginary part of the index of refraction of the deposit, derived from VASE analysis, substantiate these differences. Such differences in deposit optical properties explain why visual comparisons are not directly comparable. The ability of VASE analysis to discern these differences circumvents the issue associated with translucent deposits going un- noticed by visual evaluations and invalidates the long held assumption that darker infers more deposit. Although no correlation with field issues, VASE measurements on internal injector parts from accelerated rig testing provide a qualitative basis for understanding fuel composition trends in producing internal injector deposits.

DEGRADATION OF DIESEL IN A MODERN FIE SYSTEM

Christopher R Smith, Kesavan Gopalan, Christopher J Chuck and Christopher D Bannister

Trends in the automotive industry in recent years to reduce emissions and fuel consumption have led to diesel vehicles utilising injection systems capable of increasingly higher pressures, with typical peak rail pressures above 2000 bar now common. At the same time fuel composition has been changing around the world to meet legislation, most notably with the increased use of biodiesel. Since the introduction of biofuel regulations, FAME has been implicated in fuel degradation and filter blocking, which can cause fuel starvation and vehicle breakdown. However, more recently there has been growing concern that the increasing pressures and concomitant temperatures the fuel is exposed to in modern vehicles can itself be the cause diesel degradation, even with the absence of bio components. A rig which simulates the pressures and temperatures that a fuel is subjected to in a modern vehicle was used to investigate the issue of fuel filter blocking. It was found that at a rail pressure of 2000 bar both B0 EN590 and B10 (SME) diesel caused filter blocking to the same degree. This implies filter blocking caused by on board fuel degradation has the potential to occur broadly in a wide range of different fuel compositions independent of bio content. Further testing on the B10 fuel with a rail pressure of 2000 bar resulted in a pressure difference across the fuel filter of 0.5 bar within 200 hours, whilst the corresponding experiment at 1000 bar showed no filter pressure increase. Using a simplified diesel fuel, filter blocking was observed at both 2000 bar and 1000 bar rail pressures, however with the lower pressure blocking occurring in over double the period of time. This work concludes that the increases in rail pressure of modern diesel engines have a significant effect on the propensity of vehicle diesel filters to block.

ADVENTURES IN DIESEL STABILITY: STANDARDISING THE QUARTZ CRYSTAL MICROBALANCE METHOD

David J. Evans, Renée L Webster, Paul M. Rawson, Nathan Matheson and Christy-Anne Stansfield

Diesel stability requirements in the fuel specifications have a sole focus around trying to predict the “use by date” of the fuel. This requirement has greater relevance for organisations that tend to hold fuel for extended durations versus the retail sector. Additionally, changes in fuel system design such as high pressure common rail injection fuel systems have placed greater emphasis on the ability of diesel fuels to resist thermal oxidative processes. Current diesel fuel specifications do not include a thermal stability requirement. Current storage stability tests such as ASTM D2274 and D5304 are well established however these were validated solely on high sulfur fuels. These tests have not been good at identifying problematic fuels versus newer methods such as the rapid small scale oxidation test (RSSOT) and quartz crystal microbalance (QCM). QCM testing of a range of ultra-low sulfur diesel fuels showed that the fuels are low sediment formers producing generally less than 2 µg/cm2 of deposit in 15 hours. The fuels were all observed to be fast oxidisers with the 90% of available oxygen being consumed at various rates. In order to assess the stability of the fuels a method of standardising the QCM results was investigated. This paper will discuss the methods used and relationships between stability and oxidation products formed.

CARBONACEOUS INTERNAL DIESEL INJECTOR DEPOSITS: MECHANISMS, CHARACTERIZATION, AND REMEDIATION

Andrew McKnight, Jim Barker, and Jacqueline Reid

As the global diesel vehicle base continues to shift to high pressure common rail engine technology to meet ever stricter emissions legislation, the result is a heightened sensitivity to deposit formation. A significant industry focus on internal diesel injector deposits over the last decade has generated significant knowledge on contributing factors. Several primary deposit types have been identified. One such type, carbonaceous deposits, is inherently a concern because it is derived from thermo-oxidative breakdown of fuel inside the vehicle instead of fuel-borne contaminants. This paper will provide examples where these deposits have been found, explanation of the formation mechanism and characterization techniques, fuel effects, and effectiveness of deposit control additives to remediate these deposits.

SESSION 5: AVGAS and GASOLINE

A NOVEL APPROACH FOR THE EVALUATION OF THE DEPOSIT FORMING TENDENCIES OF SPARK-IGNITION FUELS

Seven R. Westbrook, George R. Wilson, III

As plug in, hybrid automobiles with range extending onboard generators increase in popularity, so does the concern over the storage stability of motor gasoline. The concern is because gasoline will oxidize to form gums and other compounds that can cause deposits in the engine. A range extended hybrid vehicle is more vulnerable to this problem since gasoline could remain in the fuel tank for several months if the engine is not often used. This paper will review potential new and/or testing methodologies and protocols which may be required in order to properly evaluate both the risk of unwanted deposits and approaches to mitigate the problem.

OXIDATION STABILITY OF HIGH OCTANE UNLEADED AVIATION GASOLINES FOR USE IN GENERAL AVIATION

Cunping Huang and Sneha Gollamudi

Aviation gasoline (AVGAS) is a vital element of the piston engine aircraft safety system. Approximately 167,000 aircraft in the United States rely on 100 low lead (100LL) AVGAS for safe operation. 100LL is also the only remaining transportation fuel in the United States that contains the tetraethyl lead (TEL) that has been used as an AVGAS additive for decades to create the very high octane levels required to prevent detonation (engine knock) in high power aircraft engines. Operation with inadequate fuel octane can result in engine failure and aircraft accidents. The Federal Aviation Administration (FAA) and industry formed the Piston Aviation Fuels Initiative (PAFI) to utilize industry experts to support an FAA process that identifies unleaded AVGAS candidates, provides for the generation of qualification and authorization data on those fuels, supports fleet-wide authorization of the most promising AVGAS and facilitates deployment of those fuels throughout the industry. PAFI evaluation and testing will assess the viability of candidate fuels in terms of impact upon the existing fleet, production and distribution infrastructure, environment and toxicology, and economic considerations. Fuel oxidation stability is one of the important topics of the PAFI program. The success of this research will provide the deeper understanding necessary for the development of unleaded aviation fuels for general aviation. Fuel gum formation is a thermodynamically spontaneous oxidation process (auto-oxidation). Organic components in fuels have varying tendencies for gum formation depending on their oxidation activation energies when reacting with oxygen in air. As an autocatalytic process, fuel gum formation can be accelerated by metal ions (Cu2+, Mn2+ etc.) and organic peroxides (RO-O-) formed in the initial state of a fuel sample. Increase of peroxide concentrations will lead to increased gum formation rate, reduced heat content and the loss of fuel anti-detonation performance. Although fuel gum formation mechanisms for various fuel components are different, the overall process follows a similar pathway: beginning with organic peroxides, proceeding to fuel oxidation intermediates (aldehydes, acids, resins), and ending in poly-organics (gums). This research addresses insoluble gum formation during fuel oxidation stability tests of unleaded fuels using the ASTM D873-12 (Standard Test Method for Oxidation Stability of Aviation Fuels). Along with gum measurements, elemental analyses of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) are carried out for potential gum analyses. Fuel oxidation kinetics is investigated using two-dimensional gas chromatography and high sensitivity and resolution time of flight mass spectroscopy for the detailed oxidation intermediates and byproducts analyses. Fuel density, vapor pressure and viscosity are also monitored as physical property changes during fuel oxidation.

SESSION 6: ALTERNATIVE AVIATION FUEL

IMPACT OF AROMATIC TYPES AND QUANTITIES ON O-RING POLYMERS

Mickaël Sicard, Jacques Ancelle, Bruno Raepsaet, Frédéric Ser

In 2015, during the previous IASH symposium, we presented the results obtained on the impact of the jet fuel chemical composition on O-ring polymers. 5 fuels obtained by blending a Jet A-1 with a SPK fuel 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… In the case of the nitrile O-rings, the aromatic content has an important impact on the mechanical properties. More surprising, we showed evidence of the same matter loss for all the tested fuels, it is mainly obtained during the 14 first days of the soaking tests. We also highlighted particulates in the liquid phase. For the fluorosilicone and fluorocarbone O-rings, the aromatic content seems to have less influence.

Blending fossil jet fuels with SPK fuels allows decreasing the aromatic rates but it also impacts the amount of other products like cycloalkanes, sulphur compounds, phenols… Thus, with these blends not only the rate of aromatic compounds is studied. That is the reason why a second approach was also proposed. SPKs were blended with an aromatic cut representative of the one found in jet fuels but also with a mono-aromatic cut, a di-aromatic and a bicyclic aromatic compound. The aim of this work was to determine the impact of the quantity and type of the aromatic compounds on polymers. The results show that the nitrile O-rings are the most affected by the fuels. The more the quantity of bicyclic compound is, the more the volume swell and the mass gain are. Moreover, a partial dissolution of the o-rings is observed with the apparition of particles in the fuel liquid phase.

EXPLIC PROGRAM: IMPACT OF AROMATIC CONTENT IN DIFFERENT ALTERNATIVE AERONAUTIC FUEL EMISSIONS

D. Delhaye, J. Ancelle, M. Sicard1, L. Jing, and I.K. Ortega

In the period up to 2030, global aviation is expected to grow by 5 % annually according to International Air Transport Association IATA (Lee et al. 2010). The aviation industry has identified the development of biofuels as one of the major ways it can reduce its emissions from fossil origin. With an increasing number of alternative fuels available, there is a need for a systematic method to evaluate how the chemical composition of different fuels affects their emissions. Complete engine tests are technically and economically challenging. In this work, we have used a novel Combustion Aerosol STandar (CAST) Generator especially designed to work with few amount of liquid fuel (Jing et al. 2003) to study the emission generated by up to 15 different fuels: JetA-1, Synthetic Paraffinic Kerosene (SPK), Aromatic Fluid (AF) 450 (a mixture of 3 aromatic representative cuts found in a jet fuel, AF 100, 150 and 200), SPK/JetA-1 blends (4 and 8 % aromatic contents (AC)), SPK/AF 450 blends (4, 6, 8 and 20.6 % AC), SPK/AF 100 blends (8 and 20.6% AC), SPK/AF 150 blends (8 and 20.6 % AC) SPK/AF 200 blends (8 and 20.6 % AC) and SPK/1-Methyl-naphthalene blends (8 and 20.6 % AC). We have measured the total number and size distribution of particles produced by these fuels at different flame richness (between 0.5-1.6), both at the raw exhaust and after treatment by a catalytic stripper coupled with a Dekati Engine Exhaust Diluter (DEED, Dekati oy) to remove the volatile fraction.

EVAPORATION AND IGNITION OF ALTERNATIVE FUELS - EXPLIC PROGRAM

O. Rouzaud, J. Garraud, R. Lecourt, C. Lempereur, M. Orain, G. Illac, M. Sicard

The EXPLIC program is an ONERA in-house project about the characterization of alternative fuels ranging from the material compatibility to the ignition. It aims at studying specifically the influence of aromatics cut and paraffinic cut on the fuel behavior. On the aromatics part, we consider different blends of a Synthetic Paraffinic Kerosene (SPK) mixture with, either a mono-aromatics cut or a di-aromatics cut. On the paraffinic part, we modify the paraffinic compound distribution. In both cases, influence of the initial composition has also been investigated. The paper focuses on the evaporation and the ignition of these alternative fuels, and comparisons with the Jet A-1 data are provided. Although these two phenomena are not related to a specific

ASTM norm, they are of paramount importance when studying an aeronautical combustion chamber. The evaporation process has been studied both from an experimental and a numerical point of view with nine different fuels, including Jet A-1. The experimental device corresponds to a monodisperse droplet stream with a piezo-electric plate injecting droplets vertically upwards. To enhance vaporization, the liquid fuel is heated up to 70 °C and droplet ignition is carried out 30 mm above the injection. Evolution of the droplet surface is consistent with the expected volatility of the fuels. On the numerical side, the objective is to investigate the accuracy of the isolated droplet model with respect to the experimental data. The composition of each fuel is approximated by a limited number of species, representative of each family present inside the fuel. Comparisons with the experimental data are provided. Ignition process has been characterized with the MERCATO experimental test rig. This test rig enables to reproduce high altitude relight conditions. In the EXPLIC project, the operating conditions correspond to a pressure close to 0.6 bar, air and liquid fuel temperatures respectively around 233 and 293 K, and a mass flow rate of 0.19 kg/s. For the aromatics part, the experimental results prove that the nature of the aromatics compounds (mono- or di-aromatics) and the initial composition modify the minimal value of the fuel mass flow rate required for ignition compared to that of the Jet A-1. The most important effect is due to the nature of the aromatics compounds. For the paraffinic part, the work is in progress and will be presented at the conference.

SESSION 7: MICROBIOLOGY

USE OF ILLUMINA 16S rRNA NEXT GENERATION SEQUENCING TO INVESTIGATE ANAEROBIC BACTERIAL COMMUNITY COMPOSITION IN ENVIRONMENTAL AND FUEL ASSOCIATED WATERS.

Giovanni Cafa, Lisa Offord, and Joan Kelley

Sulfate-Reducing Bacteria (SRB) are anaerobic microorganisms that use sulfate as an electron acceptor, generating hydrogen sulfide (H2S) as the product of anaerobic respiration. SRB also create problems when metal structures are exposed to sulfate-containing water. The interaction between water and metal creates a layer of molecular hydrogen on the metal surface which SRB then oxidize while creating hydrogen sulfide, this contributes to corrosion. The oil industry can be affected by generation of toxic H2S and corrosion mediated by SRB in locations where fuel becomes contaminated with water (particularly sea water), e.g. fuel storage tanks, fuel tanks of marine crafts, or legs of oilrigs. Therefore, the detection of SRB-contaminated fuel sources becomes critical, requiring analytical and quantitative assays to detect the microbial content. The objective of this study was to employ Illumina 16S rRNA Next Generation Sequencing to investigate differences in the bacterial community composition (BCC) of three selected anaerobic samples: Sludge from fuel associated water, Seawater (estuary mud), and Freshwater (pond mud). The data was then compared with results from traditional growth tests for the presence of SRB and the effect of two liquid media Postgate’s B (PGB) and Postgate’s C (PGC) on the BCC was investigated. PGB and PGC were also investigated at two different incubation times: 2 days vs 9 days. Fuel associated water and Seawater showed a similar BCC, which differed from the BCC of Freshwater. Overall, the latter was the least diverse of the three samples, and mostly consisted of Clostridia (74.5%). Clostridia were amongst the most variable taxa observed in the 3 environments. Similarly, Clostridia showed large variability in Fuel with PGB and PGC. Longer incubation time (9 days vs 2 days) caused an increase of Clostridia, which was due to the development of Blautia spp. A Similar trend was seen in Freshwater, and similarly in Fuel with PGB after 9 days of incubation.” The use of next generation sequencing illustrated the selective pressures brought about by the use of some isolation and growth media.

ADVANCED MOLECULAR TOOLS FOR THE DETECTION AND MITIGATION OF FUEL BIODETERIORATION

Oscar N. Ruiz and Thusitha S. Gunasekera

Microbial growth in fuel is a complex issue that negatively affects the fuel’s quality and properties, and degrades fuel system performance and lifetime. Thus, it is important to develop effective methods for detection, prevention, and mitigation of biocontamination in fuel. Here, we discuss a three prong approach that focuses on early detection, nanofiltration and advanced biocides to prevent fuel biodeterioration. In the area of detection and risk assessment we present the development and use of quantitative lateral flow assay based on broad-range fluorescent peptide biorecognition elements (BREs) for detection of microbial contamination in fuel. BREs were designed to target conserved cell surface determinants of hydrocarbon-degrading microorganisms. The assay was simple to perform and demonstrated good linearity and high sensitivity. The BREs may also be used to biofunctionalize optical and electrical transducers to develop effective biosensors for fuel applications. The second approach entails the development and use of an advanced biocide that targets adaptive mechanisms required for microbial proliferation in fuel including efflux pumps, porins and membrane phospholipids. The biocide is effective at very low concentrations (≤1ppm in the fuel), can be applied directly to either the fuel or the tank water bottom, and is safe to people and the environment. Finally, to prevent microbes from entering the fuel system, strategies based on filtration present a potentially attractive approach. However, to trap microorganisms filters with sub-micrometer size pores are required and they can dramatically decrease fuel flow rates and increase backpressure. We have developed a graphene oxide (GO)- based filtration media that relies on microbe-nanomaterial surface interaction, not on size exclusion, to filter out microbes in fuel with a 99.97% efficiency while maintaining rapid fuel flow. By combining better detection methods with advanced filtration and biocides we can ensure the future integrity of our fuel supply.

FACTORS AFFECTING THE PRECISION OF FUEL MICROBIOLOGY TEST METHODS

Frederick J. Passman, PhD, Joan Kelley, PhD, and Pat Whalen, PE

Determining the precision of fuel microbiology test methods presents several unique challenges relative physical and chemical fuel property tests methods. To illuminate the impact of bioburden variability on test method variability, two ASTM interlaboratory studies (ILS) – Method D7687 Method for Measurement of Cellular Adenosine Triphosphate in Fuel, Fuel/Water Mixtures, and Fuel-Associated Water with Sample Concentration by Filtration and D8070 Method for Screening of Fuels and Fuel Associated Aqueous Specimens for Microbial Contamination by Lateral Flow Immunoassay – were performed on a single set of 192 samples. Although preliminary ILS had demonstrated that each method's variability was negligible, the full ILS results indicated substantial repeatability and reproducibility variation. However, >80% agreement between the two methods was observed. These results suggest that bioburden variability, rather than inherent test method variability, is the primary source of variation when ILS test plans are run in accordance with ASTM D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

THE RELATIONSHIP BETWEEN MICROBIOLIGICAL CONTAMINATION IN WATER PHASE AND FUEL PHASE IN JET FUEL SYSTEMS AND ITS DETECTION BY INDUSTRY STANDARD METHODS

Gareth J. Williams & Graham C. Hill

Microbial growth may occur wherever any water accumulates in aviation fuel tanks and systems and it can lead to operational problems. Because it is difficult to keep aircraft fuel tanks completely free of water, IATA recommends microbiological monitoring to ensure systems remain free of contamination. IATA guidelines also recommend that every effort is made to recover and test water in tank sump drain samples but this is not always possible. There are three IATA-recommended microbial test kits for detection of microbial contamination in fuel samples; IP 613/14 / ASTM D7978-14, ASTM D7463-16 and ASTM D8070-16. Each of the kits detects and reports microbial growth in a different way and varies in its approach to testing water phase if present in a sample, for example either testing water and fuel phase combined or testing each phase independently. IATA guidelines provide contamination limit values for each method, for fuel and water phase tests, which are indicative of negligible, moderate or heavy contamination. This paper reports on work investigating how the extent of microbial contamination in fuel and water phases influences the results obtained using these kits and will enable a better basis for establishing contamination limit guidelines.

SESSION 8: FUEL TESTING AND TEST METHODS – Section 1

COMPARISON OF PARTICULATE CONTAMINATION MEASUREMENT TECHNIQUES IN DISTILLATE FUELS

Thomas G. Smagala, Camden Cook, Andy Ye Yuan Chen, Krege M. Christison

As technology for vehicles, aircraft, and engines has advanced, original equipment manufacturers have pushed for tighter specifications on the cleanliness of the fuels that go into such equipment. The size distribution of particulate matter in fuel is important because many sophisticated modern engines have smaller and smaller clearances for the fuel to pass through at higher speeds and pressures, in particular the diesel injectors. There are existing test methods for measuring the total amount of particulate contamination in distillate fuels, such as ASTM D6217 Standard Test Method for Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration" and ASTM D5452 "Standard Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration." However, these methods fail to indicate the particle size distribution. Various laboratory instruments and test methods exist for determining particle counts in distillate fuels, but they fail to indicate the total gravimetric particulate contamination. With some assumptions about particle geometry, one can estimate the total particulate concentration in distillate fuels from the integration of the particle size distribution as determined by particle counting techniques. These estimates come quite close to the measured total gravimetric techniques which require the filtration of one liter to one gallon of fuel. Thus, a particle counter test, which consumes much less fuel, can provide an estimate of the total particulate contamination in addition to the particle size distribution.

EVALUATION OF PARTICLE COUNTING AS A VALID TOOL TO DETERMINE THE FILTRATION EFFICIENCY

Robert Pawlik, Tom Muzik, and Lewis Wolfe

This study evaluates the potential of using particle counters as a useful tool to determine the efficiency of filters in aviation fuels. Currently, there are two ASTM standard methods used to evaluate the cleanliness of aviation fuel. ASTM D2276(1) is a gravimetric method and ASTM D7619(2) method uses particle counting to determine the fuel contamination level. The study looked at the correlation between the theoretical contamination level of jet-A fuel, gravimetric and particle counting methods while flowing fuel at 50 gpm through a filter separator. Parker Hannifin's automatic particle counter (ACM20) was used for the study. Water was added upstream of the pump to increase the free water content to 5 ppm, 10 ppm, 15 ppm and 20 ppm. Also, the contamination levels were increased to 0.25 mg/L, 0.50 mg/L, 1.00 mg/L, 1.50 mg/L. The sampling ports were upstream and downstream of the vessel allowing for evaluation of the filter/separator system. In the second part of the study two particulate filters with nominal rating of 1 micron and 10 micron respectively were used. The correlation between the standard methods and filter efficiency was determined. During the study it was observed that the results from automatic particle counter correlated well with the increase in the contamination level of dry fuel. It was observed that when dry fuel was used the particle counter was a good instrument to use to observe and quantify the difference in the efficiency of the two filters used.

RECENT DEVELOPMENTS IN THE D3241/IP323 THERMAL OXIDATION TEST

Michael C Croudace

Since 2014, D3241 has introduced new standards for evaluating heater tube deposits in Annex 2 and 3 of the method. Rather than a simple visual comparison of the deposit’s color to ASTM color codes in a visible tube rater box, the tubes are analyzed systematically for deposit thickness via interferometer or ellipsometer analyses. These results are graphically represented and digitally stored for general comparison by experts. The graphs are precise enough to see the variability from test to test and instrument to instrument. This paper will describe the types and size of these variations with variety of fuels and instruments and what these observations mean about instrument controls that will improve consistency.

NOVEL AUTOMATED SYSTEMS FOR ON-SITE FUEL STABILITY AND COMPATIBILITY TESTING ACCORDING TO ASTM D4740

Didier Pigeon

Bulk fuel stored for long periods can become unstable the asphaltene content can precipitate out of solution causing the formation of sludge. This has the potential to block filters and pipes, leaving tanks with an unpumpable residue. Once a fuel has chemically broken down there is no way to satisfactorily reverse the process. Precipitated asphaltene cannot be re-dissolved. The marine fuel market is undergoing complex and far-reaching change, largely as a result of a growing body of environmental legislation. Issues surrounding fuel stability and compatibility have never been more relevant, especially with the new 0.10 per cent sulphur level for fuels used in Emission Control Areas (ECAs). Although incompatibility is not a common phenomenon its likelihood increases in tandem with fuel switching, such as when entering and leaving an Emission Control Areas (ECA). Compatibility problems must be treated as a critical concern as the fuel systems can become paralyzed. The ability to test on-site, at the point of use, enables engineers and facilities managers to conduct fuel analysis quickly and easily. Detecting out-of-spec fuels can identify potential problems before equipment damage occurs. Dedicated compatibility / stability kits exist but those kits are manual. Those kits can be used on- site. They are operator time consuming and the result relies on the operator skill. The presentation will describe a new automated system that perfectly mimics the difference phases described in D4740. The automated instrument is contained in a rugged case. The test can be carried on-site by unskilled personal in strict accordance with the test method. The built-in computer and software analyses the spot image and reports quick and solid results.

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Gareth J. Williams & Graham C. Hill

Microbial growth may occur wherever any water accumulates in aviation fuel tanks and systems and it can lead to operational problems. Because it is difficult to keep aircraft fuel tanks completely free of water, IATA recommends microbiological monitoring to ensure systems remain free of contamination. IATA guidelines also recommend that every effort is made to recover and test water in tank sump drain samples but this is not always possible. There are three IATA-recommended microbial test kits for detection of microbial contamination in fuel samples; IP 613/14 / ASTM D7978-14, ASTM D7463-16 and ASTM D8070-16. Each of the kits detects and reports microbial growth in a different way and varies in its approach to testing water phase if present in a sample, for example either testing water and fuel phase combined or testing each phase independently. IATA guidelines provide contamination limit values for each method, for fuel and water phase tests, which are indicative of negligible, moderate or heavy contamination. This paper reports on work investigating how the extent of microbial contamination in fuel and water phases influences the results obtained using these kits and will enable a better basis for establishing contamination limit guidelines.

SESSION 8: FUEL TESTING AND TEST METHODS – Section 2

FAME IN JET FUEL: A NOVEL ANALYTICAL TEST METHOD BASED ON LASER MID-INFRARED SPECTROSCOPY

Bernhard Siebenhofer, Michael Martl, and Wolfgang Ritter

The recent development of Quantum Cascade Laser (QCL) technology gives rise to new analytical methods in the field of mid-infrared laser spectroscopy. The high spectral power density of QCLs enables the analysis of liquid fuels with enhanced sensitivity and selectivity compared to conventional methods such as FTIR. This presentation introduces an innovative approach to the detection of low levels of Fatty Acid Methyl Ester (FAME) in jet fuels. FAME or biodiesel has been in focus of the aviation industry and pipeline operators in the last years. The surface active FAME has become a major concern due to increased usage in the supply chain and the potential cross-contamination of subsequently transported jet fuel. In this presentation we plan to review a novel jet fuel test method for the concentration range from 10 mg/kg up to 400 mg/kg FAME. This broad range will facilitate measurements in respect to changing FAME limits for Jet-A and Jet-A1 standards. Furthermore, FAME from different feed stocks was reliably detected, while jet additives above their specified limits did not lead to false positive FAME detection. For industrial application the test method was implemented in a rugged and portable stand- alone FAME analyzer with high sample throughput and rapid measurement capabilities. This fully automated device allows on-site jet fuel screening, as well as equipping laboratory staff with a reliable tool to quantify FAME levels in jet fuels. Data from preliminary industry studies and method development will be presented.

UNDERSTANDING PRECISION ISSUES WITH SINGLE TEMPERATURE TESTING BY ASTM D3241

George R. Wilson, III

When the industry last visited the precision of single temperature testing by ASTM D3241, the results were very discouraging. Despite efforts by the precision study participants to quantify the results as much as possible, the aviation industry decided to maintain the method in a form without a stated precision. The ensuing quarter century has seen significant improvements in the test equipment and, more importantly, a revolution in deposit rating that is moving the evaluation process from subjective to objective. This paper discusses the roots of the precision issue, observes how the methodology has steadily improved and offers fresh insight in how to make the single test temperature evaluations more meaningful. The key factor in understanding single temperature precision for the test will be shown to be limiting the analysis to the temperature range up to, and including, the Breakpoint temperature.

APPLICATION OF CHEMOMETRIC METHODS TO DEVOLVE CO-ELUTING PEAKS IN GC-MS DATA

Jeffrey A. Cramer, Mark H. Hammond, and Thomas N. Loegel

Fuel chromatography is inherently limited by the high complexity of petroleum fuel compositions. In practice, almost none of the fuel constituents are fully resolved from other components. This is due to a combination of 1) insufficient peak capacity for the large number of individual components within time and chromatographic efficiency constraints and 2) insufficient resolving power of the stationary phase in the gas chromatography column relative to the many structurally similar isomers or homologs present in fuel. Multidimensional approaches, longer columns and slower heating rates can offer some benefits but will not necessarily fully resolve previously co- eluting fuel compounds. Furthermore, the manual selection and fine-tuning of existing data deconvolution algorithms to optimize results for any given data collection would be overly burdensome to end-users in most realistic applications. This presentation will cover the development of novel peak deconvolution strategies suitable for automated use with a variety of data sets.

SELECTIVE ISOLATION OF CYCLIC SULFIDES FROM JET FUEL AND THEIR CONTRIBUTION TO FUEL OXIDATION RATES.

Paul Rawson and Sylvester Abanteriba

A novel method for selective isolation of cyclic sulfides from aviation fuels has been developed. The method is based on ligand exchange chromatography using silica gel loaded with copper sulfate. The distribution and type of cyclic sulfide was further elucidated using gas chromatographic techniques with the dominant species observed being thiophanes, thianes and dihydro benzothiophenes. Two representative saturated cyclic sulfides were selected for thermal stability assessment using a quartz crystal microbalance technique, where rapid oxidation rates in a model fuel was observed.

SESSION 8: FUEL TESTING AND TEST METHODS – Section 3

DEVELOPMENT OF A NEW AUTOMOTIVE FUEL FILTER TEST METHOD INCORPORATING VIBRATION AND CYCLIC FLOW TEST PARAMETERS

Larry Hollingsworth and Gary Bessee

Currently, many fuel filters are evaluated using ISO 19438, Diesel Engine – fuel filters – Multi-pass method for evaluating filtration performance of a filter element. This method evaluates the test filter under steady conditions, e.g., steady flow rate, no controlled vibration input, and constant temperature. OEMs have requested improved test methods to include dynamic inputs because they are experiencing wear issues and do not feel the current methods provide adequate assessment for selecting filters for their vehicles and equipment. A new fuel filter test method is under development by SwRI for the heavy-duty vehicle class. This method includes multipass filtration efficiency with particle counting, an analysis of the structural dynamics of a spin-on fuel filter, vibration input to the filter, and flow rate changes. An envelope of operating parameters for this class of filters was first defined. Second, a dynamic model of the filter was used with modal testing to identify potential structural resonances. Third, effects of structural resonance modes and flow cycling on filtration efficiency were evaluated using multipass filtration efficiency tests. The culmination of the project will be to complete a test procedure and evaluate candidate filters.

COMPARISON BETWEEN SAE J1488 AND ISO 16332 DIESEL FUEL WATER SEPARATION TEST METHODS

Gary Bessee and Kristi Rutta

Currently, ISO 16332 is in the final approval stages, while SAE J1488 is a mature test method. These methods are the two standards for automotive diesel fuel water separation utilized by most OEMs and diesel fuel water separation manufacturers. This paper will discuss the differences in philosophy for the two methods and share comparison data, as well as highlight the major differences in the performance and water removal results. Differences in test fuel and creating "standardized" biodiesel test fuel will be discussed as well as the development background for the creation of the standardize biodiesel fuel. The paper will also discuss differences in interfacial tension (IFT), microseparometer, and water droplet size distributions.

FUEL CONTAMINATION SPECIFICATIONS BY ASTM D5452 GRAVIMETRIC, MIL-DTL-2261D LIGHT OBSCURANCE (JF-WA1-NP), AND LASER PARTICLE COUNTER ASTM D7619, COMPARISONS AND PERFORMANCE REVIEW, FUTURE POTENTIALS.

Alan J. Fougere

In 2016 D-2 Inc. developed a new version of its JF-WA1 Free Water in fuel by chemical pad detection instrument to also allow a provision for measuring solid contaminates in fuel. The modified instrument incorporates a second detector below the original filter pad plane allowing measures of the amount of light that can be passed through a filter membrane. A differential dual filter technique is then used to determine the "total particulate" in mg/L. This type of light obscurance measurement of particulate in light distillates has an established history in the US DOD, reference MIL-DTL-2261D. The original technique also used two filters which are placed together through which a known volume fuel sample is passed. The particulate contamination is collected on the top filter while both filters are color stained by the fuel. Subsequent to fuel filtering a light is shown through each pad separately and the total transmission radiance is measured, the radiance difference through the two filters is then computed. The difference in radiance has been shown to be directly proportional to total particulate (mass) loading of the fuel sample. The new D-2 unit has been optimized around a 47 mm 0.65 um pore size cellulose filter, which yields higher resolution at lower contamination levels. This presentation includes trial data and precision estimates from this new instrument. The trial data includes multiple fuel types, along with data from other particulate contamination methods including laser based particle counters and the ASTM D5452 gravimetric method. A recent study performed under the auspices of the US Army TARDEC group at the SWRI laboratory in St. Antonio, TX using the three method illustrates the performance of each method against know water/dirt fuel concentrations and how the three measure perform in relation to each other in terms of setting fuel contamination levels.

SESSION 9: FUEL PROPERTIES AND EFFECTS – Section 1

NEW SULFUR REDUCTION TECHNOLOGY AS SOLUTION TO INCREASINGLY STRINGENT SULFUR REGULATIONS

Zhenning Gu, Ksenija Babic, Paul Biggerstaff, Don Wolfe, Jerry Weers, Waynn Morgan

Sulfur concentrations in liquid fuels are increasingly more stringently regulated all over the world. An example of this is the recent implementation of the US Environmental Protection Agency's (EPA) Tier 3 gasoline regulations requiring that the average sulfur content of the refiners' gasoline pool be reduced from 30 ppm to 10 ppm or less. Regulatory requirements like Tier 3 force refiners to explore more flexible sulfur reduction technologies beyond hydrodesulphurization. This paper introduces newly developed sulfur reduction technology that combines chemical solutions with mechanical processes to achieve effective sulfur reduction in various light hydrocarbon streams. The innovative approach enables complex sulfur compounds not removed by conventional refinery caustic washing to be effectively extracted in a customized combination of specialty chemicals and mechanical equipment. The technology provides enhanced flexibility in blending light hydrocarbons into gasoline while remaining compliant with the Tier 3 gasoline regulation. Results from case studies will be shared to present efficacy in total sulfur reduction, based on individual sulfur species and provide an overview of how the technology is applied in the field. The unique chemical-mechanical modular technology provides a flexible and effective sulfur reduction solution for liquid fuel producers.

EVALUATION OF AVIATION FUEL PROPERTY INFLUENCES ON DIESEL ENGINE PERFORMANCE

Andy McDaniel

The United States Navy has completed qualification testing on several non-petroleum based fuels and fuel blends which exhibit a wide range of physical and chemical properties. Since Navy operations require the use of JP-5 in diesel engines during sea operations, testing experience has accumulated on a diverse set of diesel engines and engine components. Data from this wide range of hardware technology has facilitated a deeper understanding of performance risk caused by fuel properties. Identifying these performance sensitivities is a crucial step to evolving the efficiency and technical breadth of future programs that qualify changes in fuel properties. This paper focuses on the relationship between aviation fuel properties and diesel engine performance, with a primary emphasis on engine start-ability. A compilation of four non-petroleum fuel data sets derived from testing on five diesel engine models highlights the most influential combination of fuel properties affecting diesel engine performance. These data sets also highlight the sensitivity of engine designs to “worst case” fuel properties. To understand which environmental and diesel engine design factors drive susceptibility to fuel properties, an empirical model has been developed through the combination of compression ignition combustion theory and empirical test results. This empirical application allows comparison of diesel engine sensitivity to fuels based on a truncated set of engine design factors.

PENTAMETHYL HEPTANE AS A PRIMARY REFERENCE STANDARD FOR CETANE NUMBER.

Indresh Mathur and Mical Renz

Today ASTM D613 method, the engine test method, is the gold standard for determining the ignition quality of diesel fuels. When the arbitrary cetane number scale was adopted, alpha-methylnaphthalene (AMN) was assigned a cetane number value of zero and n-cetane was assigned a cetane number of 100. In 1962 a change was made to adopt 2, 2, 4, 4, 6, 8, 8 -heptamethylnonane (HMN) as the low cetane reference standard because of the issues related to the availability of pure AMN. HMN was determined to have a cetane number accepted reference value (ARV) of 15 and today the cetane number scale is defined as: Cetane Number = vol. % n-cetane + 0.15 (vol. % HMN). The low Cetane Number Primary Reference Standard, HMN (98% minimum purity) that is required is not currently available in large quantities. Also, the very small laboratory quantities that are available are cost prohibitive. The diesel fuels industry has therefore resorted to using Secondary Reference T and U Fuels which can be unstable and require a 16 lab round-robin evaluation every one to two years. Ideally, the industry requires a substitute for HMN that can be produced in large quantities at reasonable cost. Our study has shown that 2, 2, 4, 6, 6-pentamethylheptane (PMH) can be the HMN substitute. PMH can be used not only to standardize the T and U Secondary Fuel blends, but users will also have the option the to utilize blends of Primary Reference Fuel, n-cetane and PMH for cetane number determination. The authors will present the results of the study undertaken to compare the combustion characteristics of blends of HMN and n-cetane with blends of PMH and n-cetane in CFR engine using the ASTM D613 method. It has been found that PMH behaves very similar to HMN. Results of an inter-laboratory study will be presented with data to arrive at the ARV of PMH relative to HMN to justify that PMH and n-cetane can be used as Primary Reference Fuels to determine Cetane Number (CN).

DESIGN OF AN ON BOARD AVIATION FUEL DEOXYGENATOR UNIT FOR IMPROVEMENT OF FUEL THERMAL STABILITY

Ehsan Alborzi, Matthew Dwyer, Simon G Blakey and A H J M Meijer

Gas turbine fuels are thermally stressed on route from the fuel tank, through the engine, to the combustion chamber. The temperature rise in the fuel as it passes through the engine initiates a range of chemical reactions in bulk fuel which are manifested as the formation of soluble and insoluble particulates. These ultimately participate in surface carbonaceous deposition in fuel system. These changes in chemical composition can block fuel nozzles, cause disruption to the flow of fuel, and result in the breakdown in operation of specific engine components. Surface deposition initiates from bulk fuel autoxidation reactions at t< 300 °C. This work presents the experimental investigation of the use of an optimal on-board oxygen adsorbent unit to reduce the propensity of surface carbonaceous deposit formation. Improved thermal oxidation stability by oxygen removal offers the fuel to serve as a better heat sink, absorbing more waste heat from "Very High By-Pass Ratio (VHBR) engines and using the heat to benefit in the engine performance cycle. The application of oxygen adsorbents requires a careful assessment of fuel chemical composition following on fuel deoxygenation. This is primarily due to the fact that there is a trade-off between thermal stability enhancement via oxygen adsorption separation and fuel lubricity decrease as a result of polar species separation. The experimental work is supported by using quantum chemistry calculations to investigate the selective binding of oxygen by adsorbents.

SESSION 9: FUEL PROPERTIES AND EFFECTS – Section 2

ENDOTEHRMIC REACTIVTY OF HYDROCARBONS UNDER CONDITIONS RELEVANT TO HIGH-SPEED FLIGHT SYSTEMS

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

The development and implementation of advanced combustion and high-Mach propulsion systems requires advanced thermal management strategies due to high heat loads generated during flight. A potential strategy is to use hydrocarbon fuels as the primary on-board heat sink. A portion of the heat sink can be provided via fuel sensible heating (e.g., $Cp\Delta T$), which can be supplemented with 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. Therefore, a primary need is the development of viable fuel chemistry and engineering strategies to provide the required heat sink while mitigating undesirable deposit formation. Improved understanding of the relationships between fuel chemical and physical properties and engineering implementations 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, including the use of catalysts, on fuel performance. The experimental, analytical and computational methodologies employed and relevant findings will be presented.

SESSION 10: FUEL CHEMISTRY, RESEARCH AND DEVELOPMENT – Section 1

THE ROLE OF HYDROCARBON COMPOSITION ON THE THERMAL STABILITY OF AVIATION FUELS

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ABSTRACT

Advances in jet engine efficiencies and environmental concerns have lead to increased demands being placed on aviation fuel. This has driven interest in the use of alternative fuels, such as those derived from synthetic processes, in the aviation sector. This development however requires a greater understanding of the dependence of a fuels chemical composition on its thermal stability. Previous work on the oxidation mechanisms of hydrocarbons has been restricted to treating them as a general class of species. With the increased control of fuel composition that alternative fuels can achieve, it is necessary to research the role that chemical composition has on the oxidation process, allowing for the development of fuels with increased thermal stability, for use in more efficient engines. This work investigates the oxidation mechanisms for three classes of hydrocarbon commonly found in fuel with quantum chemistry techniques, using methods established for use in mechanistic organic chemistry studies. A straight chain alkane, dodecane, a cyclic alkane, decalin, and an aromatic hydrocarbon, toluene, were used to model the three classes of hydrocarbons. Our calculations indicate that aromatic and aliphatic hydrocarbons oxidise through different routes. Aromatic hydrocarbons act as antioxidants in the fuel, donating hydrogen to other hydrocarbons, thus stabilising radicals formed during the oxidation process. However, this increases their susceptibility to oxidation, and as a consequence they undergo aromatic substitution reactions to form deposits, while aliphatic alkanes oxidise through different mechanisms. The theoretical modelling work has been supported by experiments carried out on small-scale thermal stability test devices.

THE IMPACT OF ORGANONITROGEN COMPOUNDS ON THE STORAGE STABILITY OF MIDDLE DISTILLATE FUELS

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Storage stability of middle distillate diesel fuels is of utmost importance, as poor storage stability can result in formation of gums and sediment that seriously impair the usability of the fuel. Chemically reactive fuels, either by virtue of composition, incompatibility with comingled fuels, or contamination, are generally identified by standard laboratory test methods, including ASTM D2274 and D5304. However, there have been instances where diesel fuels that pass all

specification test requirements have nonetheless failed in service. One such event was reported at the 14th IASH Symposium, where diesel fuels obtained in the Western Pacific region were forming high levels of particulate materials (PM) in storage. The results of that investigation were reported to indicate that while those fuels passed all specification requirements, there may have been a causal link between the total nitrogen content and the incidence of high PM formation.

Subsequent to that work, a study has been undertaken to ascertain the role of the organonitrogen compounds in impairing the storage stability of these diesel fuels. A liquid-liquid phase extraction was developed to isolate the basic and non-basic nitrogen compounds from those fuels and the extracts analyzed by GC-NPD (nitrogen-phosphorous detection) and GC-MS. The findings of this study that will be discussed reveal a strong correlation between the occurrence of certain basic nitrogen species and the formation of high particulates in those fuels. As a consequence of these findings, it has been recommended that a focused analysis for basic nitrogen compound content be conducted whenever storage stability is a concern.

Ongoing studies are directed towards developing comprehensive organonitrogen compound maps using GCxGC with electrochemical nitrogen detection. It is anticipated that this will provide a more comprehensive understanding of organonitrogen speciation and facilitate the detection and assessment of deleterious nitrogen content.

SESSION 10: FUEL CHEMISTRY, RESEARCH AND DEVELOPMENT – Section 2

INVESTIGATION OF THERMALLY UNSTABLE AVIATION TURBINE FUELS

Zachary West, Linda Shafer, Richard Striebich, Steven Zabarnick, Timothy Edwards

Oxidative stability of kerosene based aviation turbine fuels is of critical importance to assure the longevity and optimal performance of current and future aircraft. There are a multitude of complex chemical pathways that cause poor fuel stability, but these pathways are known to be governed by trace chemical species including organically bound heteroatomic compounds, e.g., oxygen, nitrogen, and sulfur containing species. Specific “bad actors” or compounds and/or species classes that negatively impact thermal stability can vary depending on fuel production, handling, and blending techniques. We apply the latest technology in advanced chemical characterization techniques, e.g., SPE-GCxGC and GC-NCD/SCD, to examine the total and polar heteroatomic content of a few recent jet fuels from different locations across the United States. The thermal stability of these fuels was assessed using both ASTM D3241 and ASTM D7739. Thermal stability evaluations confirm the poor-to-marginal stability quality of the fuels examined. Chemical analysis shows elevated levels of heteroatomic species; however, the specific composition varies by fuel. We also report on the effects of possible treatment options, i.e., metal deactivator additive (MDA), antioxidant, the military +100 additive package, and clay treatment, to fuel thermal stability.

THE DETAILED MEASUREMENT OF FUEL HETEROATOMS BY ELEMENT SPECIFIC DETECTORS AND GCXGC-MS

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

The polar fraction of aviation fuels contains heteroatomic species which determine fuel thermal stability and oxidative characteristics. Previous work has shown that removal of this complex collection of low concentration (<1500 mg/L) polar components greatly improves the thermal stability of poor fuels, while addition of the same fraction into stable fuels significantly degrades thermal stability. While there is significant evidence that the polar fraction is a controlling factor in fuel thermal stability behavior, the low concentrations of nitrogen, sulfur and oxygen-containing components, and the complex reactions between them, make it difficult to understand the nature of the deposition forming process. The measurement of these heteroatomic compounds before and after thermal exposure is important to understanding the behavior of fuel thermal oxidation. In this effort, we use solid-phase extraction (SPE) to isolate the polar fraction and then analyze the fraction using GC with sulfur- and nitrogen-specific chemiluminescent detectors. In addition, two different GCxGC techniques using differing column configurations and detectors are used to examine the polar fractions before and after stressing in QCM and JFTOT devices. Specifically, the oxidation of sulfur and nitrogen components, the interaction of the two heteroatomic species, and the disappearance of each of these after deposition are studied. These investigations were performed in low thermal stability fuel and in model mixtures with added heteroatomic components. This work will help identify the components and oxidation processes involved in deposition reactions.

STUDIES OF THE ROLE OF HETEROATOMIC SPECIES IN JET FUEL THERMAL STABILITY: MODEL FUEL MIXTURES AND REAL FUELS

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

Although conventional petroleum-derived jet fuels primarily (>99%) consist of hydrocarbons, there are a number of important properties (e.g., lubricity, electrical conductivity, storage stability, and thermal stability) which are controlled by trace fuel species. These species primarily consist of heteroatomic molecules, with very small amounts of dissolved metals (< 1 ppm). Previous work has shown the role of oxygen-containing heteroatoms, such as phenols and hydroperoxides, in fuel autoxidative thermal stability. Phenols have been shown to inhibit oxidation but increase surface and bulk deposit formation. Hydroperoxides are autoxidation products at relatively low temperatures (<120ºC) and rate-controlling reaction intermediates at higher temperatures (≥140ºC). Sulfur-containing species have been shown to be detrimental to fuel thermal stability but, conversely, provide important fuel lubricity properties. Nitrogen species have been studied less frequently with conflicting results – some nitrogen species greatly increase deposition while others are relatively innocuous. Most previous work studied heteroatomic species in isolation rather than as mixtures of heteroatomic species classes, as occurs in actual fuels. A relatively small number of studies have explored the interaction between heteroatomic species during fuel autoxidation. In this study we utilize oxygen consumption and deposition measurements of model fuel mixtures and real fuels to explore the role that heteroatomic fuel species, and their interactions, play during fuel autoxidation. A range of temperatures, oxygen consumption regimes, and flow environments are employed to provide results applicable over a wide range of fuel autoxidative conditions. The quartz crystal microbalance (QCM) provides a low temperature (140 ºC) static reactor environment for long reaction times (minutes to hours) with oxygen consumption and sensitive in-situ deposition measurements. The JFTOT system provides a flowing environment at higher temperatures (260 to 300 ºC) and short residence times (seconds) which we have modified with an outlet oxygen sensor measurement and quantitative deposition measurements via ellipsometry and/or interferometry. These techniques are used to study model systems (Exxsol D80 with added heteroatom species) and real fuels to determine the role of heteroatomic species in jet fuel autoxidation and deposition.

SESSION 11: FUEL CHEMISTRY, RESEARCH AND DEVELOPMENT – Section 3

UNRAVELLING THE DETAILED COMPOSITION OF OXIDIZED JET FUELS: AN ORIGINAL DETAILED MECHANISM OF TOLUENE AUTOXIDATION

Detlev Conrad Mielczarek, Mickael Matrat, Arij Ben Amara, Laurie Starck

Aromatics are key components of conventional and alternative transport fuels as they contribute to high octane number in gasoline fuels and are required for materials compatibility in aviation context. However, they are being pointed out as precursors of combustion particles and fuel system deposits. In this study, a detailed kinetic mechanism was developed for toluene liquid phase oxidation, selected as a surrogate compound for jet fuels aromatics. The mechanism generation was based on an open source automated mechanism generator (RMG) associated with quantum chemistry calculations for thermochemical parameters estimation. Original experiments were carried out to validate the mechanism, involving induction period measurements using PetroOxy from 403-433K and major liquid-phase oxidation products monitoring using Gas Chromatography-Mass Spectrometry. The model allows to predict the induction period within one order of magnitude and reproduces oxidation key pathways and major toluene autoxidation products, such as benzyl alcohol, benzaldehyde, benzoic acid and cresols, in agreement with literature. This study provides a methodology associating automated mechanism generation and quantum chemical calculations to address aromatics autoxidation. This opens the way for a better assessment of the detailed composition of oxidation products and deposit precursors. Further work will be dedicated to different aromatic surrogates representative of aviation fuels and aromatics/alkanes co-oxidation.

WALL ROUGHNESS EFFECTS ON DEPOSITION OF THERMALLY STRESSED AVIATION FUEL

Phil Gadsby and Simon G. Blakey

Thermal instability in aviation fuels has been quite thoroughly explored over the last 50 years. The problem is somewhat complex, with coupling of chemistry, heat transfer and fluid dynamics. Most efforts have been applied to the chemical kinetics of deposit formation and studies of physical effects such as temperature, flow rate and Reynolds number in a multitude of small to large scale testing devices. Much less attention has been paid to the effects of wall surface roughness. This is surprising, since for turbulent flows, wall roughness enhances heat, momentum and mass transfer between the wall and the free stream, reduces the extent of the laminar portion of the boundary layer, modifies the boundary layer velocity profile and depending on the type of roughness, interferes with turbulence structures responsible for transfer of particles to and from the wall. Furthermore, a rough surface increases the wall surface area, potentially presenting more active sites for metal catalytic activity and increasing fluid residence time in and around roughness troughs. Two types of roughness were investigated - principally the roughness created from additive manufacturing (an important consideration for engine manufacturers) and drawn microscale tubing. In some cases with high relative roughness (around 4%) and turbulent flow, the deposition rate was doubled with respect to the ‘smooth’ case. However for other cases, a minimal effect was observed.

GAINING A FUNDAMENTAL UNDERSTANDING OF FUEL PERFORMANCE THROUGH ADVANCED CHEMICAL COMPOSITION MEASUREMENTS

Robert E. Synovec, Chris E. Freye, and Matthew C. Billingsley

Kerosene-based jet and rocket fuels such as Jet A, JP-8, RP-1, and RP-2 are ubiqitous to the aerospace propulsion industry. There is an ongoing need to more fully assess the fuel composition (i.e., specific chemical compounds and compound classes present as a result of refining and feedstock blending) for the purpose of improving quantitative connections between fuel composition, properties, and ultimately system performance. Prediction of fuel performance through modeling puts a greater emphasis on obtaining detailed and accurate fuel property and compositional information. In order to optimally glean chemical composition information from complex fuels, we apply comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC x GC – TOFMS). By applying multivariate data analysis techniques, referred to as chemometrics, we have readily correlated the chemical information for a broad compositional range of distillate or multicomponent aerospace fuels (50+) based upon their GC x GC – TOFMS data, to data obtained from the same fuels using ASTM standard measurement methods that infer fuel performance properties (e.g., density, viscosity, heat of combustion, and so on). In addition to correlating chemical information with thermodynamic and transport properties, application-specific performance metrics such as thermal stability are readily correlated and predicted. Specifically, data acquired from a state-of-the-art fuel performance testing platform referred to as Compact Rapid Assessment of Fuel Thermal Integrity (CRAFTI) will be presented, providing insight into how fuel thermal integrity depends upon chemical composition. This research platform has broad implications for the development of high fidelity composition-property models, leading to an optimized approach to fuel formulation and specification for advanced engine cycles.

POSTER SESSION

IDENTIFICATION AND QUANTIFICATION OF OXIDATION PRODUCTS OF FUEL COMPONENTS ANALYSED BY MASS SPECTROMETRY

Marcella Frauscher, Nicole Dörr, Charlotte Besser, and Alexandra Rögner

Oxidative stability is an important issue in respective fuel specifications to support storage stability. However, applied thermo-oxidative test methods provide fragmentary evidence of the fuel´s oxidation stability as either the volatiles (e.g., open set-up EN ISO 12205) or the liquid phase (e.g., rancimat EN 14112) are not considered. Typically, degradation degree is determined by conventional analytical methods such as neutralization number, infrared spectroscopy or determination of water. Thus, chemistries of degradation products remain hidden although the knowledge of the chemical structures and amounts formed from certain product classes may explain specific oxidation behavior and hence support product development. In order to observe all degradation products – both volatile and liquid – and their respective quantities at different degradation degrees, a custom-design artificial alteration was applied. Model jet fuel mixtures were artificially altered in a closed vessel pressurized with oxygen at 95 °C. Degradation products in samples taken during this procedure were analysed by gas chromatography mass spectrometry(1). Oxidation products were unambiguously assigned to the most relevant chemistries (i.e., alcohols, aldehydes, ketones, and acids) and quantified with different methods such as selected ion monitoring. Methodology developed enables the qualitative and quantitative determination of the degradation products that dominate fuel degradation. Furthermore, sampling during the stability assessment procedure allows monitoring how oxidative attack of fuel components proceeds over time, hence time-related information on the type and amount of degradation products on the molecular level can be gained. Moreover, variation of alteration parameters (e.g., temperature) as well as addition of commonly occurring impurities (e.g., fatty acid methyl esters) allow the systematic evaluation of such influencing factors on fuel degradation.

LABORATORY TEST RIG WITH MINIATURE TURBOJET ENGINE AS A TOOL FOR TESTS OF ALTERNATIVE AVIATION FUELS

Jarosław Sarnecki, Bartosz Gawron, Tomasz Białecki

Aviation is one of the fastest growing types of transport. Increasing number of aircrafts during recent years is associated with higher intensity of aviation operations carried out. This causes increasing demand for fuel, being power supply for turbine engines, and leads to increase of harmful products which are produced during combustion process. Emitted pollutants, such as harmful exhaust gases, particulate matters and volatile organic components have negative effect on climate, air quality and human health. In today's research more and more space is devoted to issues related to reduction of harmful emissions from aviation into the environment. Many international research programs are aimed at developing new and greener solutions for aviation industry. One of major considered methods of harmful combustion products reduction is introduction of various components to fossil fuel, including biocomponents and biofuels.

However, analysis and measurements on full scale aircraft jet engines are complex and expensive. Moreover, quantities of biofuels especially obtained from experimental installations are limited. Air Force Institute of Technology, being leading research organization in Poland within fuels for aviation, creates specialized research facilities. In the Department of Fuels and Lubricants laboratory test rig with a miniature turbojet engine (MiniJETRig – Miniature Jet Engine Test Rig) was designed. The test rig has been developed for research aimed at modelling and investigating processes or phenomena occurring in full scale turbine engines. Small volume of fuel is required to carry out tests, which is the main advantage of miniature turbojet engine application. The paper presents construction of a test rig with brief description of its main components functionalities. Methodology and results, in term of performance and emissions of miniature turbojet engine for few tested fuels (e.g. HEFA fuel) are shown. Measurement results are compared with data for neat Jet A-1 fuel. The main research applications of MiniJETRig is testing of alternative aviation fuels. In paper, others applications and capabilities of the test rig are shown. For example, the test rig is used for assessment of combustion products impact on living cells.

SCALE DOWN OF DEWAXING PROCESS

Milena Mantarro, Viviana Berto, Danilo Zufferli

Dewaxing aids is the definition given to the chemicals able to interact with the feed paraffin, modifying the wax crystals during the dewaxing process. Compared to the baseline without additive, the benefits given by the use of the dewaxing aid are an increase of the throughput (production rate) and dewaxed oil yield, with a consequent positive impact on the refinery’s margins. Test were performed applying an internal procedure based on a laboratory scale simulation of the dewaxing process. The feed was diluted in a solvent mixture and cooled at a fixed rate up to the selected temperature. Then the cooled feed was filtered on a filter resembling the one used in the dewaxing plants. The applied conditions were selected based on those normally applied in the plant. The performances of the additives were evaluated based on key parameters. Different applications of dewaxing aids in the plant were allowed to validate the method developed in the laboratory.

INVESTIGATION OF COMPATIBILITY BETWEEN HFO AND LSFO IN MARITIME INDUSTRY AND THE EFFECT OF STABILIZING ADDITIVES USING FUEL STABILITY ANALYZER (ASTM D 7157)

Milena Mantarro, Viviana Berto, Antonio Guarascio

In 2015 IMO regulations set new limits at 0,1% sulfur content of fuel oil in Emission Control Areas (ECA), which presents a significant challenge for the whole maritime industry. Under the revised MARPOL Annex VI, the global sulphur cap will be reduced from current 3,5% to 0,5%, effective from 1st January 2020. When ships pass through an ECA, they have to switch to an ultra low sulphur fuel oil (LSFO) or other low sulfur fuel, later, when they leave it, they switch back to HFO to avoid extra costs. Switching from one type of fuel to the other is a delicate operation and it can lead to incompatibility problems. Adding a fuel oil or distillate (Low Sulphur) with a predominance of paraffinic hydrocarbons to a heavy fuel oil (HFO) with a high asphaltene content can promote the precipitation of asphaltenes as sludge, causing the clogging of filters which may cause the engine to shut down. This paper reports a series of compatibility tests between HFO e LSFO in different ratio. All the tests were performed with a Fuel Stability Analyzer, in compliance with ASTM D 7157 and have shown incompatibility problems between the fuel oils analysed. The study shows how the fuel oil stability blend can be improved, avoiding the flocculation of asphaltenes, when blended in certain ratios with the use of some stabilizing additives.

MICROBIOLOGICAL CONTAMINATION OF FUEL – TREATMENT MANAGEMENT FROM STORAGE TANKS TO WASTE WATER SYSTEM AND ON FILLING STATION

Marco Buccolini, Silvia Bozzi , Valter Tandoi

Since when the presence of Biodiesel in mineral fuel became mandatory, problems related with the presence of microbiological growth and biofouling are becoming more and more evident in storage tanks, in refinery depots and in filling station. Possible consequences for the filling stations in terms of maintenance and cleaning are quite relevant and can even lead to the stopping of the operation with significant economical loss. The use of the microbiological treatment set up by Chimec S.p.A., properly managed according to the operative (and environmental) conditions, is the most versatile solution, allowing to get rid of the contamination problems in tanks, refinery and/or filling station without any problems for the waste water biological system (WWTP). A study together with CNR shows the impact of the use of two different Chimec biocides on a sample of waste water activated sludge, detecting the value of EC 50, applying the standard method ISO 8192: 2007 based on the measurement of oxygen consumption by activated sludge. The determination of the EC 50 value combined with mass balances in the WWTP, allow to do the biocide treatment in safety conditions, without compromising the WWTP performances. The study on monitoring the EC 50 values (at 0,5 and 24 hours contact time) with different chemicals have been performed with the target to demonstrate the non toxicity of different biocide chemicals on the activated sludge, the most common wastewater treatment process, utilized: both products belong to the 4th class, with EC 50 > 100 mg/L. On the other side, to have a complete vision from all the sides of the plant and facilities involved in microbiological contamination, a procedure developed for the cleaning of the tanks of filling station, affected by microbiological contamination, based on the combination of two different chemicals, is reported. This procedure was experimented on true filling station on the Italian distribution net, allowing to clean the fuels from microbiological contamination, avoiding the wasting of fuels and the segregation of the tanks and a loss of economical revenue. In this paper the modern biomolecular tools utilized for microbial contaminants characterization (Fluorescent in situ Hybridization and PCR) will be shown together how the Chimec know how contributes to manage and control all the production and supply chain involved in microbiological contamination of fuel blended with biofuel form renewable raw material.

ISSUES WITH NEW RAW MATERIALS AS FEEDSTOCKS IN BIOFUEL

Stefano Cacciatori, Silvia Bozzi

Critical feedstocks such as UCO (Used Cooking Oils), nowadays are becoming more and more interesting for the production of biodiesel, especially after the issue of the European Directive 2015/1513 which set a cap of 7% of energy in transport in 2020 for the biofuels from food crops. The UCOs are listed in the part B of the Annex IX, among the raw materials that can count twice their Energetic content, except for different internal rules applied by the Member State. Moreover a biodiesel produced from UCOs can indeed guarantee GHG emission savings (EU amendment 2015/1513) higher than 80%, fully complying with the new European requirements also for new installations. For this reason there is a growing interest in their use as feedstock for biodiesel to be blended in mineral gasoil. A critical point of these UCOs is the high variability in quality and characteristics, being related to the composition of the base oil (palm, seeds, tallow…) and to the frying conditions (temperatures, frying cycles, type of food fried, etc.). The use of this new raw material as blendstocks for mineral diesel often has an impact, in terms of filterability, cold properties, oxidation stability, on the base properties of the mineral fuels and requires the evaluation of new chemical physical properties and new test method. The aim of this study is to highlight some considerations on the use of this raw material, especially UCOs in the production of biodiesel and on its treatment with specific additives. All the considerations are based on Chimec's experience in this field.

MICROBIAL CONTAMINATION IN ROAD VEHICLE DIESEL-A SURVEY OF GAS STATION UNDERGROUND TANKS IN TWO US STATES.

Joan Kelley and Gerry Herman

The occurrence of microbial contamination in gas station storage tanks in two states was compared. Florida and New Jersey were selected as regions with contrasting climates and the work was carried out on stations belonging to the same company across both states during a 2-week period in May/June. Testing was carried out on-site using kits compliant with ASTM D8070. Samples were taken from as close to the tank bottom as the design allowed. Access was gained through the tank fill point and where possible samples were also taken via the Submersible Turbine Pump (STP) access point. Where contamination was found in the storage tank, nozzle samples were also tested for potential carry over. Positive microbial contamination was defined as that giving results considered 'moderate' or above as indicated by the test kits. A total of 101 tank and nozzle samples were tested from 45 gas stations, 22 in Florida and 23 in New Jersey. In New Jersey 40% of fill end samples contained a water bottom, 50% in Florida. 51% of fill end samples were contaminated in New Jersey and 50% in Florida. In New Jersey 75% of STP end samples contained a water bottom, 71% in Florida. 63% of STP end samples in New Jersey were contaminated and 71% in Florida. In New Jersey 32% of the nozzle samples tested contained detectable carry over contamination while this rose to 67% in Florida.
Overall, in New Jersey 74% of the sites showed contamination and 50% in Florida giving 62% contaminated sites over the 2 States. Although the percentage of tanks with visible water was approximately the same in both states, significantly more of these sites were contaminated with microorganisms in New Jersey than in Florida. Visible water presence did not always correlate with contamination. Carry thru of contamination into nozzle samples was significant and

greater than anticipated at the start of this project. While trend analysis is normally the preferred method for characterizing microbial loading in fuel tanks. This was a snapshot study carried out in response to repeated reports of blockage and corrosion in 30µ filters. The paper discusses the results in full.

COMPARISON OF ASTM METHOD D8073-16 (SMALL SCALE WATER SEPARATION METHOD) WITH REAL FILTER COALESCING PERFORMANCE BY SINGLE ELEMENT TEST STAND WATER MAPPING

Alan J. Fougere, Ian Mylrea, and Paul Wells

This paper describes the correlation of a new test method, ASTM D8073-16, with water separation characteristics of coalescing filters for aviation fuel. False negative water separation tests in the jet fuel supply chain have significant impacts on aviation fuel distribution, causing disruption and increased cost. By false negative we mean that an aviation fuel which does not meet the required level of result (85, or 70 if containing SDA) and is therefore predicted to have bad water separation characteristic's, actually has good water separation characteristics when passed through the latest design water separator. This can be understood because new 5th edition filter materials outperform materials previously employed for water separation methods, hence test results from existing methods don't always predict filter water separator field performance. The new method uses EI 1581 5th Edition filter material to coalesce the water, which is typical of filter water separators currently employed, and hence is likely to correlate better. A comparison with full scale field filter performance was carried out using the Single Element Test (SET) Water Mapping Protocol previously presented at IASH in 2011 [Wells/Hoskin] to see how the new method compared to existing methodology and how well the new method correlated with the field filter results. A discussion on the results for both weak and strong surfactants and additive blends is provided.

IDENTIFICATION OF OXIDISED COMPOUNDS IN AVIATION FUELS USING NAFION FIBRE SOLID PHASE MICROEXTRACTION

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

Thermal stability of aviation fuels is a key consideration facing the operation of high-performance aircraft. As modern aircraft engines and fuel systems are required to operate at increasingly high temperatures and employ fuel as a coolant for hydraulic and avionics systems, fuel thermal instability and oxidation reactions are of growing concern. Thermal oxidation occurs when fuel hydrocarbons react with dissolved oxygen, leading to the formation of various oxidised species from hydroperoxides. This is problematic as these oxygenated species are known to attack engine components(1) and form solid deposits leading to blockages and increased frequency of maintenance(2). Identification of oxygenated compounds is an important aspect of assessing the serviceability of the fuel, and to formulate strategies to mitigate the effects of the oxidised species. However, identification of oxidised species in fuels is complicated by the complex nature and matrix interferences that may arise, and the low concentration of the compounds of interest(3). Nafion SPME fibres were prepared and applied to the analysis of oxygenated analytes in non- polar aviation fuel matrices. The performance of the Nafion fibres was investigated and exhibited high extraction efficiencies for polar analytes compared with a commercially available polar fibre. Calibration curves were constructed for several oxygenated compounds with linearities up to 0.999 for concentrations of 10-100 mg/L. Oxygen containing compounds were also identified from thermally oxidised aviation fuels using single column and multidimensional gas chromatography with mass spectrometry.

DETERMINATION OF IGNITION DELAY AND LEAN BLOWOUT LIMITS OF NARROW DISTILLATION PROFILE ALTERNATIVE FUELS USING A SMALL GAS TURBINE

Ulas Yildirima, Glen Rowlinsonb, Sylvester Abanteribaa and David J. Evansb

Precise determination of Ignition Delay (ID) and Lean Blowout (LBO) characteristics of alternative fuels remains elusive to the fuel community. Currently, test methods exist in the determination of the ID times of fossil and alternative fuels, which require various laboratory apparatus in an attempt to emulate real life scenarios as part of the test methods. Notably, most available data is based on empirical data obtained from fossil fuels. There have been reports that for certain types of alternative fuels these tests fail to provide useful results. The harshest operating environment for any turbine fuel is within the combustor of a gas turbine. In this experiment, a small gas turbine has been modified and the engine control unit redesigned in order to determine ID and LBO limits of a number of narrow distillation profile alternative fuels.

SINGLE JFTOT TESTS FOR UNDERSTANDING THE BREAKPOINT OF A FUEL

David J Abdallah, Kenneth E. Thompson, Scott K Berkhous

The current methodology for determining distillate fuel thermal stability margin involves performing multiple ASTM D3241 measurements at different set point temperatures in order to determine the breakpoint temperature. This process is impractical for routine testing and often can take days to perform. A single test capable of assessing a fuel’s thermal stability is described that takes the same amount of time to run as a standard single D3241 test. The enhanced breakpoint methodology is conducted at an elevated temperature and utilizes deposit metrology to evaluate the deposit thickness profile. The tube axial position where deposit reaches a thickness limit or deposit slope limit is correlated to the D3241 Appendix X2 breakpoint temperature.

PREPARATION, STABILITY AND PROPERTIES OF WATER-EMULSIFIED JET FUEL PREPARATION, STABILITY AND PROPERTIES OF WATER-EMULSIFIED JET FUEL AT LOW SURFACTANT CONTENT

Moshe Rabaev and Reuven Falkovich

Adding water vapor into the combustion process of fuels, while difficult, holds great promise for improving combustion characteristics, reducing unwanted products and providing an “antiknock" effect. The process of creating emulsions of water in JP-8 fuel for concentrations of water and surfactant lower than 2% has been studied. Surfactant combinations were found which created clear, stable or quasi-stable emulsions with maximal water: surfactant ratios of 0.75-1.9. A critical micelle concentration of 0.10-0.15% was found for one of them. Low-temperature behavior was studied, and a reversible clouding phase transition was observed between -10 and -20°C which is possibly the freezing of "bound" water. In general, easily-measurable clouding point was found to be sensitive to different phase changes in dilute micelles. Two operational properties of the fuel were tested and the emulsions were found to have little to no effect on either foaming or bulk pour point. Effects of both water- soluble (alcohol) and fuel-soluble (ester) co-surfactants were noted. These results demonstrate a promising direction towards improving upon existing jet-fuel and turbine engines.

A STUDY ON THE STABILITY OF MARINE DISTILLATE FUEL IN THE PRESENCE OF FAME AND HVO

Chrysovalanti E. Tsesmeli, George S. Dodos and Fanourios Zannikos

The upcoming International Standard EN ISO 8217:2016 refers to the addition of biofuels, such as FAME and HVO, in distillate marine fuels and includes additional specifications for DF grades (DFA, DFZ, DFB) containing FAME up to 7% v/v. Notwithstanding the benefits arisen from biofuels, potential implications regarding the stability of distillate fuels may appeared. Due to its high affinity to water and the tendency to oxidation, FAME is often associated with microbial growth and storage stability issues. Additionally, in spite of the limited available literature data regarding the use of HVO in marine distillate fuels, the latter may also be considered as a renewable substitute. Taking the aforementioned into account, the introduction of bio- derived fuels in marine industry provokes great interest on investigating their impact on marine distillate fuels stability. The aim of this study was to investigate to what extent the addition of FAME or HVO affects their microbial and oxidation stability of marine distillate fuels and whether they have an impact on marine fuel systems. In specific, FAME and HVO were blended with a distillate fuel used widely in marine industry at the concentration of 7% v/v. Two different arrays of contaminated microcosms along with non- contaminated ones have been set up and stored for a certain period of time under specific conditions in order to examine the behavior of these two biofuels. At predetermined intervals of storage time the microbial proliferation was monitored by the ASTM D7687 method. The oxidation stability was assessed both by the RSSOT (ASTM D7545) and Rancimat (EN 15751) methods which are considered as more suitable for assessing the aging reserve of fuels containing bio-based derivatives. Basic fuel quality parameters were also examined at the end of storage period in order to determine any alterations due to the presence of each biofuel. Moreover, the effect of FAME and HVO in the compatibility with a variety of representative metals was assessed.

UPDATE ON EI 1535 WATER MAPPING TEST METHOD

Keri Petersen1 and Gary Bessee

After the introduction of the water mapping test protocol to EI 1535 3rd edition in 2015, SwRI is investigating what other factors may impact the results of the test. Since the EI 1581 qualified coalesce/separators are operating outside their designed parameters, a study will be conducted at Southwest Research Institute to evaluate the differences and repeatability in results using filter elements from different manufacturing batches and filter elements from different manufacturers. This study will use an additive with an historical known performance. Two different batches of EI 1581 5th edition coalescers and separators will be ordered from multiple manufacturers. On each test day, elements from each manufacturer will be tested to eliminate variation caused by the fuel. At the end of the test program, these results will be added to SwRI's historical database of results to evaluate the repeatability of results with manufacturer and batch variation, as well as evaluate any notable trends in the results.

PHENOL IN AVIATION FUEL MONITORING ON IP583 / ASTM D7797 EQUIPMENT

Paul Spitteler

The primary use for the IP 583 / ASTM D7797 "FAME In Jet Instrument" is to screen aviation fuel for the presence of FAME contamination. Infrared spectra are collected from the sample and the sample stripped from polar components by a sorbent material. In addition to FAME other components like phenols are retained on the sorbent material and therefore show up in the absorbance spectrum constructed from the sample and the processed sample. Hindered phenols that are generally used as antioxidants are not effectively captured in this system and therefore have no significant impact on the resultant spectra. The phenols that are observed in the spectra are the ones that find their way into the fuel during the refining process. This paper discusses the construction of a Partial Least Square model to determine phenol concentrations in aviation fuel from spectra obtained to determine FAME concentrations. This opens the possibility of developing a system to monitor phenol concentrations which involves no hardware modification and only a software addition to the IP583 / ASTM D7797 test. The spectral region of interest is shared with alcohols and the infrared spectra of phenols vary significantly with the phenol side groups and this poses some challenges to the model. Phenol concentrations in typical aviation fuels can be of the order of several hundred ppm. The reference data used in this study was obtained from a newly developed HPLC extraction method developed by ExxonMobil to distinguish between various phenols and measures their concentrations.

MICROBIAL CONTAMINATION TEST METHODS IN BULK FUEL STORAGE

Marlin Vangsness

The goal of this DLA Energy funded study is to evaluate low (normal) and elevated levels of microbial contamination in bulk storage of government owned fuel. Fuel was drawn from multiple sampling locations and tested using several off the shelf test kits as well as an AFRL developed procedure. Readings were compiled according to fuel type, test location, and test method. Preliminary observations on the variability in test results for microbial contamination in bulk fuel storage are reported.

FUEL COMPOSITION-TO-PERFORMANCE STUDIES AT THE UNITED STATES AIR FORCE RESEARCH LABORATORY'S FUELS AND ENERGY BRANCH

Edwin Corporan

Recent research efforts at the U.S. Air Force Research Laboratory to study the impacts of fuel composition on combustion performance metrics are described. Investigations include: 1) effects of fuel chemical and physical properties on lean blowout, combustion efficiency and ignition at low temperatures in a single nozzle swirl-stabilized combustor, 2) ignition delay studies of relevant jet fuel chemistries in a shock tube, and 3) studies of primary fuel pyrolytic decomposition products and their potential correlations with fuel combustion performance. The fuels evaluated consist of two-component surrogate blends (containing n-, iso-, cyclo-paraffins and/or aromatics), certified synthetic fuel blending formulations, and a conventional jet fuel with average properties. The selected fuels provide a wide range of chemical and physical properties, to help provide insight into their impact on performance. The combustion devices provide data at relevant turbine engine combustor environments and at conditions focusing only fuel chemical kinetics effects (shock tube). Potential correlations of combustor and shock tube performance with fuel physical and chemical properties, fuel reactivity, and primary product selectivities of the thermally cracked fuel are discussed.

COMBUSTION TESTING OF CANDIDATE ROCKET FUELS: OVERCOMING SPECIFICATION CHALLENGES THROUGH SUBSCALE EVALUATION

Matt Billingsley

Aerospace fuels are produced to meet specification limits imposed for the most part by engine operational expectations. Ideally, these metrics are representative of the intended application, guaranteeing fuel quality regardless of production method or source (conventional or alternative). In practice however, complex processes like combustion and regenerative cooling are sensitive to fuel compositional variability not directly controlled by specification tests. For example, chemical variation among several within-specification, highly refined rocket kerosene fuels was recently shown to drastically impact cooling system material compatibility and reliability. From a combustion standpoint, although thermochemical (e.g., heat of combustion and hydrogen content) and physical (e.g., viscosity and density) characteristics are commonplace in fuel specifications, verifying application-specific combustion behavior is not feasible with current test methods. Furthermore, while engine-level evaluation is ideal for confirming fuel fit-for-purpose quality, it is overly expensive and time consuming. In such cases, subscale testing is often employed to evaluate candidate fuels in controlled environments at a low cost, thereby verifying fuel performance and overall fit-for-purpose quality. This presentation summarizes progress of an experimental campaign in which several candidate kerosene-based rocket fuels were tested in a subscale rocket thrust chamber. Performance characteristics will be reviewed with the purpose of drawing connections between specification properties and system-level behavior. Through this effort, we intend to identify potential deficiencies in the current rocket kerosene specification regarding fuel combustion in future aerospace platforms.

ASSESSMENT OF THE ROLE OF COPPER CONTAMINATION ON DIESEL FUEL STORAGE STABILITY

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

It has been shown in the past that high levels of copper are often found in stable F-76 diesel fuels, however there have also been isolated incidents where very unstable F-76 fuels have been found to contain high levels of dissolved copper. Recently, there have been incidents where F-76 diesel fuels from west coast refineries have produced unacceptably high levels of insolubles in storage. In order to help determine whether copper may be either responsible or a contributing factor to poor storage stability, experiments were performed to assess these issues.

A series of storage stability experiments were conducted on various F-76 diesel fuels including low sulfur diesel, ultralow sulfur diesel and high sulfur diesel. Controlled concentrations of dissolved copper were obtained by blending each fuel with the same fuel that had been exposed to copper turnings. Copper concentrations were verified by ICP-AES analysis in accordance with ASTM D7111. Tests were conducted with various copper concentrations with and without a metal deactivator additive. The impact of blending downgraded copper contaminated JP-5 into stored diesel fuel onboard Navy ships was also examined by testing blends of these diesel fuels with copper contaminated JP-5. Copper concentrations in these fuel samples ranged from 65 ppb to about 800 ppb in the neat samples. The samples were stressed according to ASTM D5304, ASTM D4625 and ASTM D7525 in order to gain a broader understanding of what may be occurring in these fuels during storage. During these storage stability tests, total insolubles and hydroperoxides were determined, and GC-MS analyses was conducted to detect any significant chemical changes.

INTRODUCING ASTM METHOD D8071 for PIONA COMPOUND ANALYSIS BY GC-VUV

Dan Wispinski

Measurement of bulk composition of hydrocarbon groups and individual compounds in automotive spark-ignition fuels is important for quality control as well as ensuring compliance with various governmental regulations. As such, multiple ASTM methods exist for measuring various aspects of automotive fuel samples. Most of the methods are limited in scope to a subset of hydrocarbon groups or specific compounds of interest, meaning that multiple methods are required for typical production control. During the December 2016 D02 committee meeting ASTM International approved method D8071 for PIONA compound analysis by GC-VUV, known also as the “Standard Test Method for the Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive Spark-Ignition Engine Fuel using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV).” The method uses relatively simple instrumentation: a gas chromatograph, a standard 30 m nonpolar column, and a vacuum ultraviolet (VUV) absorption detector. VUV absorbance exhibits sensitivity to all major hydrocarbon classes that occur in automotive spark-ignition fuels, has a high degree of speciation capability, but also exhibits the intuitive property that species belonging to similar hydrocarbon groups have similar absorption characteristics. The setup procedure is straight-forward, with no pre-column tuning or valve timing adjustments. The ability to perform library searches and deconvolution using the inherently three-dimensional dataset means that the new method can use a wide retention index window, so it is more forgiving of variations in retention times than are methods that rely solely on retention time for compound identification or classification. Additionally, since the new method can handle co-elution among various species and hydrocarbon classes, analysis is faster since complete chromatographic separation of all components is not necessary. The new method results in a per-measurement information set that would typically require implementation of multiple ASTM methods, while being inherently more robust and production-worthy than the more comprehensive ASTM automotive fuel methods.