13TH INTERNATIONAL CONFERENCE ON STABILITY, HANDLING AND USE OF LIQUID FUELS
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Abstract Summaries

SESSION 1: RENEWABLE FUELS

CO-HYDROPROCESSING – BIOFUEL IN MIDDLE DISTILLATES

Ulrich Balfanz, Alisdair Q Clark, Steve Anderson, Wenzel Strojek, Tuan Anh Tran

Aviation represents a unique and critical part of the global transportation system, linking the countries of the world with over 80,000 flights carrying approximately 6 million passengers per day. The Industry is built upon scientific understanding, with attention to detail for aircraft/engine design and fuel selection to deliver a high level of reliability, efficiency and performance. With environmental focus on CO2 emissions, the Industry have sought to apply these principles to meet the challenge, with targets of:

- Improving fuel efficiency by 1.5% annually to 2020
- Capping carbon emissions with carbon-neutral growth from 2020
- Achieving a 50% reduction in net carbon emissions by 2050 compared with 2005[1]

Numerous options are being progressed to meet these goals, including engine/aircraft design, flight profile optimisation, carbon trading and fuel technology. The focus of the present paper is on fuel technology, where the Industry have approved a number of aviation kerosines derived from alternative sources to mitigate CO2 emissions. Such technology is also sought by other sectors, for example automotive diesel where European Directive 2009/28/EC seeks a minimum of 10% renewable energy in transport fuels by 2020. Work is presented covering the interface between ground and aviation fuel middle distillate hydroprocessing. A selection of natural bio-oils have been co-hydroprocessed at 5% v/v in mixture with crude oil derived feed under typical refinery conditions. Such a route has already been identified as a potential way to make a hydrocarbon, renewable diesel[2] and the impact on jet fuel quality is examined using both hydroprocessing and hydrocracking conditions. Carbon bio-fuel content is allocated to diesel/kerosine by 14C dating technology with some surprising results.

HYDROCARBON RENEWABLE AND SYNTHETIC DIESEL FUEL BLENDSTOCKS: COMPOSITION AND PROPERTIES

Thomas G. Smagala, Earl Christensen, Krege M. Christison, Rachel E. Mohler, Erica Gjersing and Robert L. McCormick

The properties of synthetic paraffinic and hydrotreated renewable diesel fuels follow logically from their composition. Comprehensive two-dimensional gas chromatographic analysis with nonpolar and polar columns is a powerful technique for determining the bulk composition of

these fuels. This technique was used to determine the carbon number distributions of total, normal, and isomerized paraffins in a variety of samples, including a Fischer-Tropsch diesel from coal and hydrotreated renewable diesel fuels from vegetable oils, animal fats, and algal oils. The detailed compositions were crucial to providing deeper insight into the chemical and physical property trends. In particular, the compositions were able to elucidate the general differences in properties, such as low temperature operability, ignition delay, distillation profile, density, kinematic viscosity, and net heat of combustion. These properties in particular are crucial to predicting the successful performance of the fuels for use in compression-ignition engines. In each of the fuels, the fraction of normal to isomerized paraffins and the shape of the carbon number distributions have the largest influence on these properties.

BIOMASS PYROLYSIS OIL AS A RENEWABLE FEEDSTOCK FOR BIO-JET FUEL
Mariam Ajam, Chris Woolard, and Carl L Viljoen

Environmental and energy security concerns have stimulated interest in the development of renewable conversion technologies for transportation fuels. Fast pyrolysis of biomass is an emerging renewable energy process that has gained considerable interest as a method to produce renewable liquid fuels. Biomass pyrolysis oil is potentially an attractive renewable source of bio-jet fuel components. The biomass pyrolysis oil produced from fast pyrolysis cannot be used directly, as a “drop-in” fuel, because of its chemical and physical properties. The undesirable properties of the biomass pyrolysis oil such as high corrosivity, low energy density and thermal instability are due to the presence of a variety of oxygenates in the oil. Biomass pyrolysis oil requires upgrading in order for the resultant fuel component and/or blends to be compliant with existing jet fuel specifications and compatible with existing logistical systems and engine technology. Catalytic hydrotreatment is an upgrading technology commonly used to improve the product properties of biomass pyrolysis oils by reducing the oxygen content of the oil, amongst others. This technology involves the treatment of biomass pyrolysis oil with hydrogen in the presence of a heterogeneous catalyst. The bio-jet fuel produced from biomass pyrolysis oil upgrading is a high density fuel component with a high aromatic and cycloparaffinic content. It is hence ideal for blending with lower density Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK) and Hydroprocessed Esters and Fatty Acids (HEFA) fuels. This paper summarises the typical fuel properties and thermal oxidative stability properties of bio-jet fuel derived from biomass pyrolysis oils in comparison with crude-derived jet fuel. The stability of model compound systems, representative of a range of refractory oxygenates in biomass pyrolysis oil, are also evaluated in this paper. Thermal oxidative stability techniques used in this paper include the Jet Fuel Thermal Oxidation Test (JFTOTTM), Quartz Crystal Microbalance (QCM), static flask oxidation and the PetroOXYTM instrument. Insights into the catalytic hydrotreatment of biomass pyrolysis oil to a bio-jet fuel component are also discussed.

ADDITIVE EFFECTS ON ALTERNATIVE FUELS, IMMEDIATE AND AFTER LONG-TERM STORAGE

George R. Wilson, III, Lori Zuziak

In early 2012 thirty (30) samples of alternative fuels (FT SPK, HEFA SPK and B20) were placed into 43°C storage for 32 weeks. The sample selection included both neat and additized versions. The emphasis was on additives that offered potential benefit for US Army ground forces, biocide and cetane improvers. The materials chosen represent alternate fuel extremes. The US Army does not intentionally use B20 for tactical vehicles but it is present on some bases and in the national fuel inventory. The SPKs are not intended to be used neat but part of the routine evaluation of alternative jet fuel components has been the evaluation of their performance unblended. Each type of fuel was evaluated with the following additive combinations: Neat, Biocide, Cetane Improver(s), Biocide and Cetane Improver(s). In addition, each sample was inoculated with a live colony of microbes (plus water) added into an otherwise clean sample. Each sample was evaluated by the standard tests for the class of fuel at the start and at the end of testing. This paper is going to discuss the impact of these additives on the fuel and the impact of the storage on both.

NEXT GENERATION FUEL FILTRATION MEDIA

Dr. Sven Siegle, Dr. Máté Nagy, and Howard Yu

The demands of fuel filtration is increasing due to legistation and the impact to the environment. Achieving high performance and consistent quality is made more challenging by the different fuel quality, climate and need for cleaner fuel. There are may forms of contaminants, which needs to be addressed, from asphaltenes, salts, soaps, to microbial growth and fuel degradation products. There are standardized testing to quantify the performance of filter media for fuel systems, and trying to best correlate them to real world conditions. Important charactistics of high efficient fuel filter means good efficiency, high capacity and lifetime, good water separation, good durability and convertability at the customer end. H&V has utilized both the conventional filtration media constructions, and new nanofiber technologies, to develop media with meet the current performance requirements of customers, as well as developing new media with even higher performance levels.

BIOFUEL FEEDSTOCKS METRICS STUDY

Pamela M. Serino

The U.S. Military Services (Air Force, Army, and Navy) collectively have aggressive initiatives for the procurement of hydrocarbon fuels containing blend components derived from next generation renewable biomass feedstocks. Several recognized challenges exist in the development of applicable feedstocks for next generation biofuels regarding issues of production, sustainment and environmental impact. Drop-in biofuel feedstocks and production pathways present a variety of novel upstream sustainability benefits, considerations and concerns not considered when procuring traditional petroleum-based bulk fuels. The Defense Logistics Agency (DLA), executive agent for bulk petroleum fuels for the Department of Defense (DoD)

and military services, has sought to achieve greater awareness and understanding of operational biofuel sustainable supply chain criteria, beginning with feedstock production and processing. As the military services' demand for these operational biofuels grows, DLA Energy increasingly requires a sustainability architecture to consistently identify and evaluate these operational fuels' supply chain risks. LMI Government Consulting was contracted to develop such an architecture to serve key DLA Energy roles and business line needs germane to effective determinations and evaluations of the risks connected to biofuel acquisition and management specific to fuel feedstock origin. The tool was developed in collaboration with DLA Energy and other government agencies that have involvement in related initiatives if alternative fuel/energy, biofuel feedstock development and environmental effects (including the DOE, USDA and EPA); additionally, industry and academia stakeholder individuals and organizations contributed to the structuring of the architecture through meetings and discussions that provided additional technical feedback. The architecture framework analyzes feedstock sustainability though four basic pillars: operational, economic, environmental, and social. For these pillars, technical indicator sheets were developed with several metrics that robustly frame, assess, and manage issues of concern throughout the biofuel lifecycle. Through the application of these metrics to individual feedstocks and respective production/supply chains, risk management criteria can be established that can be integrated into the DLA Energy commodity acquisition process.

AUTOMATED INSTRUMENT TO QUANTIFY D3241 ABSOLUTE DEPOSIT USING INTERFEROMETRY (INTERFERENCE METHOD)

Didier Pigeon

In the early 1990's Robert E. Morris and Robert Wagner of the US Navy developed and patented (Patent Number 5,293,298 - March 1994) a technique that used interferometry to measure the thickness distribution and volume of jet fuel thermal oxidation deposit by scanning the length of the tube with an optical probe. At that time, the technique showed limitations in measuring deposit thickness thinner than 100 nm. The technique was abandoned because studies showed that the critical thickness corresponding to an ASTM D3241 "3" failing visual rating was in the range of 80 to 100 nm. Based on the combination of this technique and the latest UVVIS spectrometer available at present, AD Systems has developed an automated instrument that precisely quantifies the D3241 deposits from 0 up to 1200 nm. The presenter will describe the technique and detail the results obtained with the ASTM / EI interlaboratory study. Based on these results, Energy Institute published the IP 597 test method - Rating of heater tubes — Interferometric method. In addition, Didier Pigeon will present results on specific heater tubes for which visual tube rating (VTR) approach generates much debate.

SESSION 2: CHALLENGES IN FUEL DISTRIBUTION, STORAGE AND USE WITH TODAY'S AND TOMORROW'S FUELS

PITFALLS & QUALITY ASSURANCE DURING THE SUPPLY CHAIN OF BIOFUELS TO THE TRANSPORT SECTOR

Kurt Tyssen

The World Biofuels Market today is a very complex business. Different biomass sources, different supply systems, different conversion techniques requires a high demand of quality assurance throughout the supply chain from raw materials to end products like transportation fuels. Recently new developments in the Renewable Energy Directive are proposing a blending limitation with conventional biofuels and promoting the use of higher blends with new advanced bio components. On the other hand fuel quality specifications become stricter due to new engine and catalyst developments from the automotive industry, to improve engine performance, fuel consumption and exhaust gas emissions. The varied characteristics of an increasing range of feedstocks for conventional biodiesel production and trading demands rigorous testing and inspection throughout the supply chain. Parameters such as cold flow properties, incompatibility with additives, hygroscopic character of biodiesel, filter blocking issues, stability issues, etc, during transport and storage are some of the examples of these pitfalls which are leading to technical restrictions for existing fleet cars. The above pitfalls can be presented using test case examples. One of the projects Intertek was involved with was a stability study of B10 on behalf of CONCAWE. Advanced bio components such as hydrotreated, refined & Fisher Trop Refined Diesel are now entering the market. These products are very comparable with the mineral diesel characteristics, with superior performance and can be derived from waste products so there is no conflict with food chain. However distribution of biofuels and novel fuels can lead to contamination issues, therefore quality monitoring throughout the supply chain of advanced bio components is vital to the final performance of the engine. There are further concerns over the risk of non-harmonized introduction & blending across 27 different national strategies, the need for a common EU Fuel Roadmap, need for fuel specifications (in many cases test methods are lacking behind industrial developments), risk of customer confusion at the pump with multiple fuel grades and non-harmonized pump labeling in the EU.

IMPACT OF JET FUEL STORAGE ROOF DESIGN ON FREE WATER FORMATION

Paul P. Wells, Anthony Kitson-Smith

Empirical data shows high water levels in some hydrant filters and reduced service life of the filter monitors downstream of jet fuel tankage fitted with floating suctions, containing an internal floating roof cover provided buoyancy via aluminum floatation tubes. The effect is impacted by seasonal temperatures. The largest impact is seen during spring and fall, when diurnal temperature variation is largest. It is hypothesized that the thermal conductivity of the aluminum floatation tubes causes highly localized cooling and therefore more free water to separate from the jet fuel (versus other floating roof designs). Over time, the cooler, higher density jet fuel migrates downward and creates a circulation pattern within the tank. As cooler jet fuel is replaced by warmer, the process of localized cooling repeats. A "fog" created by the free water

droplets forms throughout the fuel layer. The free water droplets that are formed are of a sufficiently small size that they do not readily settle to the tank bottom. After the prescribed settling period for the jet fuel, product is drawn from the floating suction which is at the point of the proposed water generation mechanism on the underside of the floating roof. The suspended free water is found in the hydrant filter sumps, but some transmission may occur to the hydrant resulting in reduced filter monitor service life. To better understand the phenomenon and develop potential solutions, jet fuel storage tanks were simulated on a small scale. Water-saturated jet fuel is placed into large (7.5 L), clear glass cylinders with different roof designs. The cylinders were then placed into a cold room and periodically observed. Glass cylinders are used to clearly visualize the difference in free water formation. The presentation will detail the impact of different storage roof designs, materials and insulation techniques on free water formation.

MEMBRANE-BASED HYDROCARBON FUEL DEGASSING

Harry Cordatos, Ph.D.

Hydrocarbon fuels contain surprisingly large amounts of dissolved oxygen and nitrogen, as well as small amounts of water, from normal exposure to atmospheric air. Their effect on fuel system hardware is slow and insidious: from cavitation leading to pump bearing wear to carbonatious deposit formation (“varnish” or “coke”). In particular for aircraft fuel system components, carbonaceous deposits cause problems ranging from (i) sluggishness in the response of servo valves, to (ii) reduced power due to plugged fuel nozzles and heat exchangers, to (iii) in-flight engine shut-downs due to plugged “wash flow filters”, or to (iv) fuel nozzle plugging and fuel spray degradation. While these issues can be kept in check by maintaining an average fuel temperature under 250F, engine manufacturers today are under pressure to raise fuel temperatures in the design of advanced aircraft for the near future. It is therefore anticipated that deposit-related unscheduled maintenance events will become more frequent and perhaps more pronounced, since the rates of the chemical reactions responsible for their formation increase exponentially with temperature. While the mechanisms involved in deposit formation are complex, it has been established that dissolved oxygen in the fuel is a key reactant and that removing it is a very effective way to mitigate this issue. Over the last ten years, United Technologies has been active in developing a membrane-based device which can remove dissolved oxygen on-board an aircraft. Engine demonstrations have validated 600F fuel temperature capability with JP-8 by removing ~90% of the dissolved oxygen; alternatively, for applications where a 600F capability is not necessary, the deoxygenation level - and therefore size & weight of the device - can be adjusted to enable the desired fuel temperature. Moreover, since the membrane-based device can remove not only dissolved oxygen but also any dissolved gas as well as dissolved water, one can envision a variety of possibilities for engines utilizing hydrocarbon fuels. This presentation will provide an overview of the technology and experimental results to date as well as a brief discussion on possible applications and the challenges that still need to be overcome.

PREDICTION OF ODOR ISSUES DUE TO VOLATILE SULPHUR SPECIES IN HYDROCARBON LIQUIDS

Aldo Caiazzo, Ivo Dijs, and Koen Steernberg

With increasing awareness and concern on emission of hydrocarbon vapors and odors, handling of petroleum products can be challenging in locations close to urban areas. In particular the controlling of odor issues is not straightforward since trace quantities of volatile bad-smelling components can result in odor complaints already. Hence, to limit odor risks it needs to be identified what the malodorous species are, how these components are released and dispersed in the atmosphere, and which the most appropriate mitigation options are. In this paper a method is presented to predict odor risks associated to the release of traces of volatile sulfur species, which are notoriously bad-smelling components. This method makes a connection between odor threshold levels, atmospheric dispersion, and vapor/liquid equilibria. The outcome of the prediction can be used to select proper mitigation options, for example deodorant, treatment of emitted vapors, changing blend recipe, or tuning the manufacturing processes. In this presentation an example related to an odor issue will be discussed.

INTERACTION OF AROMATIC MOLECULES AND ELASTOMERIC MATERIALS: SEAL PERFORMANCE AND HANSEN SOLUBILITY PARAMETERS

Simon Blakey, Sam Kingdon, Chris W. Wilson

Elastomer seal performance in the presence of fuels can be characterized by seal swell due to the absorption of fuel into the elastomer and a reduction in sealing force due to the extraction of polymer materials into the fuel. Seal swell is known to be caused by the presence of aromatic components in the fuel. This study identifies the seal swell potential for a range of individual aromatic components and proposes some blends of aromatic components which can mimic the performance of conventional jet fuel when blended with a synthetic paraffinic kerosene. Ultimately this may allow the present minimum levels of aromatics to be reduced, paving the way for fully synthetic fuels with designed aromatic packages. Seal swell occurs as a direct result of intermolecular interaction between an elastomeric material and the fuel in which the material is in contact with. This study uses the Hansen Solubility Parameter of the fuel and seal combination as an effective way of quantifying the effects a solvent's intermolecular bonding characteristics have on the swell induced.

KEEP RUNNING: BULK DIESEL FUEL FILTRATION, WHY THE WW FUEL CHARTER MAY NOT BE CLEAN ENOUGH, AND THE IMPORTANCE OF INLET FILTRATION

Scott Grossbauer , Joseph Block, James Doyle, Brad Grove, Philip Johnson, and Paul Klick

Today’s modern diesel engines are designed with efficiency and low emissions in mind. To achieve these objectives, fuel injection system pressures have moved up in excess of 2,000 BAR. These higher pressures drive the need for fuel cleanliness levels never seen before in order to “keep running”, i.e. meet injector life and maintenance interval expectations. In order to achieve the levels of cleanliness now required, a two-step approach to filtration is needed. Onboard

filtration alone will be challenged to meet the expected levels of efficiency and life due to limitations in dirt holding capacity and compromised performance in harsh on-engine environments. This presentation will explain why bulk fuel filtration, or filtering the fuel prior to being put into use on the equipment, should be an integral part of every operation's contamination control strategy. It will also highlight why the WW Fuel Charter target of ISO 18/16/13 may not be clean enough to capture unstable fuel problems surfacing around the world. Many examples of what has caused filters to plug will be outlined, including lubricity additive, corrosion inhibitors, and cold flow improvers, to name a few. Finally, it will explain the importance of tank inlet filtration in protecting infrastructure and achieving maximum filter performance. Examples from around the world will also be shared, along with suggested best practices.

SESSION 3: AVIATION FUELS TODAY AND TOMORROW

IMPACT OF ADDITIVES ON JET FUEL THERMAL STABILITY

David J. Abdallah, Lauren Kreno, Roger G. Gaughan, Dennis H. Hoskin

The impact of jet fuel additives on jet fuel thermal oxidation breakpoints utilizing ellipsometry to quantify heater tube deposits has been investigated. Heater tube deposit metrology offers a more precise evaluation of a fuel's thermal stability. Thermal stability tests utilizing slower flow rates were also conducted to judge the fuels thermal stability under more severe conditions in cases where the breakpoint was too high to evaluate using standard conditions. The additive impact on thermal stability was minimal for antioxidants, improved for both FSII and MDA, and lowered for Stadis 450 and corrosion inhibitor. Corrosion inhibitor had the greatest negative impact and MDA had the greatest positive impact on thermal stability. In addition to improving the thermal stability, MDA altered the fuel deposit profiles significantly.

IMPACT OF GTL KEROSENE BLEND COMPOSITION ON FLIGHT PERFORMANCE OF A CESSNA CITATION II

Joris A. Melkertand Tim A. Snijders, Joanna M. Bauldreay and Paul F. Bogers

International jet fuel specifications permit up to 50% volume Fischer-Tropsch synthetic paraffinic kerosines (FT-SPKs), such as Gas-to-Liquids (GTL) Kerosene, in Jet A-1. However, having higher SPK-contents could produce desirable fuels: lower density, better payload-range performance and improved engine emissions. After a series of ground tests using GTL-containing fuels in a Cessna Citation II, with P&W Canada JT15D-4 turbofan engines, TU Delft gained permission from the Dutch aviation authorities to undertake a series of experimental flights. One engine ran on the airport's standard Jet A-1 while the other engine was fuelled with blends containing 50, 75 and 90% volume GTL kerosene. The primary purpose of the test flights was to confirm that the operability of the aircraft was satisfactory. Throughout the test programme, no problems were encountered with the fuel and fuel system. Data were collected on all relevant engine parameters. The observed decrease in fuel consumption was of the same order as the increase in fuel heating value. During the test flights, acceleration tests revealed that the engine response to throttle movement, including emergency slam accelerations, was equal for all

fuel blends. Video cameras attached to the Citation's vertical tail allowed the onset of any contrails to be captured. The contrails produced by Jet A-1 and the GTL blends showed no change in contrail onset and optical shape at cruise and climb settings. Our observations contribute to the understanding of how fuel composition and emissions at altitude, such as soot particles, create contrails under specific atmospheric conditions.

SYNTHETIC PARAFFINIC KEROSENES – IMPACT OF COMPOSITION DIFFERENCES ON JET FUEL CANDIDATE PROPERTIES

Simon Blakey, Joanna M Bauldreay, Christopher C Wilson, Ehsan Alborzi and Yue Liu

The compositional space for Synthetic Paraffinic Kerosenes (SPKS) can be mapped onto a triangle that describes a given SPK in terms of its total normal, iso- and cyclo-paraffins contents. The ASTM D7566 specification has one limit only, 15% mass maximum of cyclo-paraffins, but otherwise the SPK compositions that have been approved for blending to make Jet A or Jet A-1 are a balance between production parameters (feedstock, process, severity, etc.) and some performance parameters, such as freezing point. The Qatar GTL Jet fuel consortium set out to explore the SPK triangle, to establish where and if there were compositional "sweet spots" for one or more performance parameters. It assumed that the cyclo-paraffin limit may be unnecessary. The absence of aromatics in SPKs has been a reason to limit their inclusion in the final blends to 50% maximum, to ensure that the final fuels have adequate materials compatibility performance. However, the presence of aromatics may have drawbacks for thermal stability and combustion properties. In this paper we start by examining the elastomer compatibility of SPKs, using dynamic o-ring tests, and find that there are significant differences between zones in the triangle. The SPK results are compared with those for blends also containing model aromatics. We then examine the impact of aromatics, added as pure solvents or as Jet A-1 kerosene to SPKs, on thermal stability and the emissions from an auxiliary power unit (APU). Aromatics increase the particulate matter emissions from an APU but only cause thermal stability reductions if present as heteroatom containing molecules: it is the "fellow travelers" – e.g. oxygen, sulphur and nitrogen – with aromatics that cause stability reductions.

EFFECT OF AROMATIC CONTENT ON THERMAL STABILITY OF JET FUELS

Simon Blakey, Abdi Yusuf, Chris W. Wilson

An adapted HiReTS test rig is used for provide a small-scale research rig for the assessment of fuel thermal stability. Operating at a relatively small scale has allowed the exploration of the effect of a range of aromatic species on the thermal stability of jet fuel through the use of blended surrogate fuels from laboratory solvents and chemicals. Pure aromatic structures demonstrate a relatively small effect on the thermal stability performance of surrogate fuels, whereas the addition of small quantities of aromatic-like compounds with additional substituents containing other elements have a much larger effect. These results have significant implications for the use of an aromatic additive used to produce nitrile o-ring swelling and the production of a commercial 'drop-in' alternative aviation fuel. This result also provide evidence that it is not simply the aromatic content that leads to thermal stability related insoluble deposition but the

presence of heteroatomic species such as oxygen and sulphur containing compounds as well as fellow travelers with the aromatic stock.

EXPERIMENTAL AND MODELING STUDY OF THE IMPACT OF FAME ON OXIDATION STABILITY OF JET FUELS

Arij Ben Amara, Nicolas Jeuland, Laurie Starck, Pascal Hayrault, Andre Nicolle

Environmental concerns as well as economic and political issues triggered major changes in jet fuel formulation and quality including technological evolutions and new (bio) refining processes. These changes have affected fuel oxidative and thermal stability. Complex transport storage and blending logistics can induce fuel pollution lowering the stability of Jet fuels. Pollution of the jet fuel with Fatty Acid Methyl esters (FAME), commonly used as biofuels for road transport, is critical due to oxidation stability of these molecules. As a consequence, a very stringent limit has been set on jet fuel in order to avoid any contamination. This preventive measure can be very impacting for fuel logistic, especially for pipelines use. The kinetics of co-oxidation of jet fuel and FAME is presently poorly understood. An experimental study based on Rancimat and PetroOxy techniques has been conducted to investigate the impact of FAME addition on the oxidation stability of Jet-A1 fuel. These techniques, commonly used for Diesel/Biodiesel stability studies can bring deeper knowledge on Jet fuels oxidation kinetics. Three FAMEs of different compositions were tested over a range of operating temperatures. Results give a new insight into oxidation and co-oxidation mechanisms and the impact of the chemical composition of FAME on its promoting effect. The corresponding Arrhenius parameters were determined for Jet fuel and jet fuel/FAME blends.

EXPERIMENTAL AND MODELLING STUDIES OF THE COMBUSTION OF ALTERNATIVE AVIATION FUELS

Kevin J. Hughes, Elena Catalanotti, Mohamed Pourkashanian, and Chris W. Wilson

Jet fuels currently in use in the aviation industry are exclusively kerosene based. However, potential problems regarding security of supply, climate change and increasing cost are becoming more significant, exacerbated by the rapid worldwide growth of the aviation sector. Aviation fuels based on biofuels blended with kerosene or synthetic Fischer-Tropsch derived fuels are possible alternatives. To investigate the combustion behaviour of these alternative aviation fuels, an experimental study at a variety of stoichiometries using a flat flame burner with kerosene, kerosene/biofuel blends, and Fischer-Tropsch derived kerosene substitutes have been performed. A fine wire thermocouple measures the temperature profile of the flame, and product analysis by online gas sampling provides the major species concentrations (O2, CO2, CO) along with NOx. These measurements are complemented by the use of Planar Laser Induced Fluorescence (PLIF) to provide relative concentration profiles of NO and the reactive intermediates OH and CH. Parallel to these experimental studies, a combined chemical kinetic model of surrogate representatives of kerosene, biofuel and Fisher Tropsch synthetic fuel has been produced and validated against the experimental data obtained in these studies and also available in the literature. This validated chemical kinetic model provides a sound basis for

further work to simplify and incorporate it into computational fluid dynamic models of the performance of alternative fuels in real engines.

PRE-REFINED CRUDES AND THEIR IMPACT ON JET FUEL THERMAL STABILITY OVER TIME

Roger G. Gaughan, David J. Abdallah, Dennis H. Hoskin

Historically, jet fuel simply consisted of the straight run kerosene cut from crude oils. This endured for years while market demand remained below the average kerosene yield from a barrel of oil. As a result, the jet fuel specification was based on a straight run, or a treated (chemically or hydrogen treated) straight run, kerosene cut derived from conventional crudes. During this time, a fuel that met the jet fuel specification (e.g., D1655 or Def Stan 91-91), and remained contaminant free, could be expected to meet the specification until its consumption.

While jet fuel demand continued to increase, the kerosene portion of the crude barrel decreased due to a drop in crude quality. This combination of increased demand and decreased kerosene yield lead to pre-refined crudes (PRCs) being gradually introduced into refinery crude slates. The most notable change to jet fuel quality consisted of the inability of some fuels to maintain their thermal stability properties during storage. This fit for purpose (FFP) property has been characterized by the fuel's JFTOT Breakpoint Degradation (JBD). Jet fuels derived from PRCs may contain new deleterious molecules that will not allow the fuel to remain FFP over time.

Normal refinery processing of PRC derived jet fuels may produce on specification jet fuels; however, some may not be FFP as their thermal stability may degrade over time. This introduces the potential for a fuel to degrade and fail the JFTOT specification while being stored in the field. In an effort to mitigate the adverse effects associated with the introduction of these new deleterious molecules, refiners need to be aware of this FFP property and ensure adequate treating (e.g., Chemical or Hydrogen treating) is applied to these PRC derived jet fuels such the jet fuel maintains its expected thermal stability during storage.

JBD has been identified as a key FFP property for jet fuels derived from PRCs. A JBD protocol and FFP definition is presented, providing guidance as to how to ensure on specification PRC derived jet fuels remain FFP when stored for extended periods of time.

THE CONTENT OF THE ISO-PARAFFINS IN JET FUEL AND ITS INFLUENCE ON PROPERTIES

Zuoran Shi, Zhiping Tao

In the oil refining process, straight run jet fuel fraction accounted for only 4-8%, the shortage of the jet fuel is becoming more and more outstanding. Therefore, more and more people start to blend synthetic paraffinic kerosene with petroleum-based jet fuel. The lubricity of jet fuel is an important property. As the content of synthetic paraffinic kerosene in jet fuel increased, the composition of jet fuel changed. Consequently, the influence of the composition change of jet fuel on its lubricity and viscosity was investigated. Results indicated that the lubricity improved as the percentage of iso-paraffins in jet fuel increased. In addition, the high content and heavy fraction of iso-paraffins would lead to a big viscosity of jet fuel. However, the increase of the viscosity made it difficult to determine the smoke point, as the smoke point is very sensible to

the viscosity. Then, the smoke point of the jet fuel was studied and found that the jet fuel had to be heated to a appropriate temperature to determine the smoke point.

SESSION 4: CHEMICAL EFFECTS ON FUEL PROPERTIES

EFFECT OF FUEL CHEMICAL COMPOSITION ON SUPERCRITICAL REACTIVITY AND DEPOSITION PROPENSITY

Matthew J. DeWitt, Brian McMasters, Theodore Williams, Tyler Hendershott, Rich Striebich, Tim Edwards and Donald K. Phelps

The successful development and implementation of hydrocarbon-fueled high speed aerospace platforms require advanced concepts to enable sufficient heat sink for vehicle and engine cooling. This requirement is necessary due to the large quantity of waste heat generated at high speeds which cannot be effectively managed via indirect cooling strategies, such as with "cooled cooling air." A primary route to achieve required levels of heat sink is to use the on-board fuel as the primary coolant, where the sensible heating enthalpy is supplemented by deliberate bulk endothermic reactions of the fuel via thermal and/or catalytic cracking chemistry. However, a major limitation to viable implementation is the undesirable formation of carbonaceous deposits, which can reduce fuel flow, increase resistance to heat transfer and foul injector nozzles. Therefore, improved understanding of the effect of fuel chemical class composition and physical properties on fuel reactivity and deposition propensity is required to develop viable hydrocarbon fuels for endothermic applications. This understanding is critical since it provides insight into chemical and physical properties which control reactivity and deposition propensity and the basis for development and evaluation of advanced methodologies (materials, coatings, catalysts) to enable hypersonic applications. Experimental and modeling efforts are being performed using single components, model solvents and fully-formulated jet and rocket fuels to improve the understanding of fuel chemistry and reaction conditions on endothermic reactivity. The experimental, analytical and computational methodologies employed and relevant findings will be presented.

EFFECT OF ADDITION OF AROMATICS ON THE THERMAL-OXIDATIVE STABILITY OF ALTERNATIVE AVIATION FUELS

Matthew J. DeWitt, Zachary West, Steven Zabarnick, Linda Shafer, Richard Striebich, and Tim Edwards

There has been significant interest in the development, certification, and use of alternative (non-petroleum) aviation fuels. Extensive laboratory and full-scale testing have resulted in the approval of synthetic paraffinic type fuels for use as blending feedstocks in both commercial and military fuels. This includes Synthetic Paraffinic Kerosene (SPK) produced via Fisher-Tropsch synthesis and Hydroprocessed Esters and Fatty Acids (HEFA) from plant oils and animal fats. These SPK and HEFA blend stocks are predominantly paraffinic (normal and iso-) in composition and contain minimal aromatic and heteroatomic compounds. The neat paraffinic blend stocks exhibit favorable characteristics, such as excellent thermal-oxidative stability and significantly reduced particulate matter propensity during combustion. However, these have poor

lubricity and insufficient material compatibility/seal swell characteristics as synthesized. As a result, blending with petroleum-derived fuels to a minimum total aromatic concentration of 8% by volume is required to insure Fit-For-Purpose requirements are satisfied. This constraint reduces the beneficial aspects of the neat paraffinic fuels, also adding a logistical step. Development of Fully Synthetic Jet Fuels (FSJF), which can be used directly as drop-in replacements, is desired. A potential route to viable FSJFs is to blend SPK/HEFA fuels with aromatic compounds/solvents. Recent studies have investigated the effect of aromatics addition (e.g., petroleum and synthetically-derived) on the thermal-oxidative stability of SPKs; these have shown differing impact on the resulting fuel stability. Therefore, laboratory studies and analyses were performed to improve the understanding of the effect of aromatic addition on fuel thermal stability. Studies were performed using both batch and flowing reactor systems, in conjunction with detailed chemical analysis of bulk and trace species. A primary goal was to elucidate the controlling reaction chemistry and identify the cause for differing stability characteristics with varying types of aromatics. An overview of the various efforts will be provided and implications will be discussed.

EXPERIMENTAL AND THEORETICAL INVESTIGATION OF PATHWAYS TO DEPOSIT FORMATION IN THERMALLY STRESSED AVIATION FUEL IN THE PRESENCE OF NITROGENOUS ADDITIVES

Detlev C. Mielczarek, Simon Blakey, Kevin J. Hughes, Derek B. Ingham, Mohamed Pourkashanian, Chris W. Wilson

In new and future aircraft, an increase in the operating temperature of the engine allows for more powerful and efficient engines. As fuel is employed as the primary coolant for aircraft systems and engines, thermal stability of aviation fuel is of major concern, both in the context of conventional as well as synthetic fuels. In this paper, we present a systematic experimental investigation of the influence of nitrogen species on thermal stability. Experimental evidence obtained from a HiRETS thermal stability test rig indicates that aromatic nitrogen compounds, such as m-toluidine, have a detrimental impact on the stability of aviation fuel and lead to a significant increase in the rate of formation of deposits. A chemical kinetics model based on an autoxidation mechanism derived from an automatic mechanism generator, Reaction Mechanism Generator (RMG), has been extended to investigate possible mechanistic routes to deposit formation arising from the studied additives. Further the thermodynamic and kinetic parameters for the postulated interactions have been obtained from quantum mechanical calculations performed with Gaussian 09. We use these parameters to assess within the model, the feasibility of the postulated pathways to deposit formation.

UNDERSTANDING PHENOL LEVELS IN JET FUEL

David J. Abdallah, Frank P. DiSanzo, Roger G. Gaughan, Mark W. Genowitz, Paul P. Wells, Dennis H. Hoskin

Jet fuels may contain a small amount of phenols originating from the crudes used in their production. Phenols can increase fuel deposition when thermally stressed. They may also impact fuel system materials compatibility. Phenol levels are not routinely checked. There are only a

few reports where phenol levels in jet fuel are quantified: fuels analyzed by BP and communicated by Dacre et al. reported between 80 and 600 mg/L; a series of U.S. Air Force jet fuels analyzed by Heneghan et al. reported between 0 to 1955 mg/L; and two sweetened Jet A fuels analyzed by Kendall et al. reported 75 and 136 mg/L phenols in jet fuel. Phenol levels in jet fuel vary depending on the crudes slate selected and whether or not hydroprocessing and wet treating processes (in particular clay and caustic washing) are used. Enrichment beyond historic levels is possible with the introduction of waste water recycling (for example, using phenolic-rich spent caustic from a product wet treater for desalting crude). Enrichment can also result from the implementation of advances in refining technology. The possibility of phenol levels trending upward prompted us to start measuring them in jet fuel. We developed a preliminary analytical test that distinguishes between five groups of alkyl substituted phenols based on molecular size. The method consists of extracting phenols into an aqueous base solution followed by HPLC analysis. Using this method 70 commercial jet fuels tested in 2011 from a variety of Colonial Pipeline receipt terminals revealed phenol concentration ranging from 50 to 2000ppm with an average molecular size around methyl, dimethyl and ethyl substituted phenol. The analytical test method was further improved and applied to a second set of Colonial Pipeline samples taken from the same locations one year later. In addition, a few samples from the 1st survey are re- evaluated to understand potential bias between the methods. This report describes details of the test method, results obtained from the phenol surveys, and the efficacy of the extraction processes using phenols of known structure. Considering the difficulty in performing the analytical test, we also investigated a rapid screening test. It was found that phenols can be measured rapidly in much the same way FIJI measures FAME in jet fuel. Details of the preliminary screening, the impact of alcohols, and the impact of phenols with sterically hindered hydroxyl groups are discussed. A more thorough report of the recent development efforts using the FIJI to measure phenols is described in an accompanying paper by Stan-hope Seta who is leading this effort.

PHENOL IN AVIATION FUEL MONITORING ON IP583 / ASTM D7797 EQUIPMENT
Paul Spitteler and David Abdallah

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 Exxon to distinguish between various phenols and measures their concentrations.

SESSION 5: TESTING

DETERMINATION OF WATER DROPLET SIZE DISTRIBUTIONS IN DIESEL AND AVIATION FUELS

Gary Bessee

As water removal becomes more of a necessity in transportation systems (ground and aviation), a better understanding of the generated water emulsions is required to remove any water contamination. Traditionally, the industry only measures the quantity of water challenging a test filter and the resultant effluent to calculate the percent water removal efficiency. With more fuel additives and alternative fuels coming into the market, variations in water removal properties such as interfacial tension (IFT) are much lower than the industry traditionally finds in the field. This property has a major impact on water removal characteristics and water droplet size distribution. We have always been able to measure the IFT, and recently, we have we been able to determine the water droplet size distributions. This paper will present water droplet size distributions of various fuels with a range of IFT values to demonstrate the impact of fuel additives and alternative fuels such as biodiesel and synthetic jet fuels.

OVERVIEW OF ELLIPSOMETER AS AN ABSOLUTE WAY TO MEASURE D 3241 DEPOSIT THICKNESS

Ervin E. Schlepp, Shaojuan Yu, Michael C. Croudace

Ellipsometry is a non-contact optical technique used to measure film thickness in integrated circuits with the accuracy of nanometers. ASTM D3241 produces thin film deposits on the specimen heater tubes which are currently evaluated visually; color ratings are equated to the amount of deposition. Visual ratings have been proven very subjective. At the 5th International Conference on Stability, Handling, and Use of Liquid Fuels in 1994 a paper was presented on a study that demonstrated Ellipsometry can provide absolute measurement of ASTM D3241 heater tube deposit film thickness. Falex Corporation, in response to industry needs and using the direction from previous Ellipsometer instruments, has developed the new Model 430 Ellipsometer dedicated to measuring D3241 film deposit thickness. Specific goals for this new instrument include mimicking results of previous Ellipsometer with heater tube deposits while improving in application specific capability, ability to measure tubular specimen, measurement repeatability and reproducibility. A study was performed to demonstrate the Falex 430 Ellipsometer produced results equivalent to earlier Ellipsometers through a direct comparison of measurements of heater tube's film deposit thickness of multiple heater tube specimens. The study proved that the Falex 430 Ellipsometer provides comparative results. Further in this study, the reproducibility and repeatability of the Falex 430 Ellipsometer was shown to be superior to earlier Ellipsometers and new ways to treat the results from this instrument can produce a significantly better deposit analyses. Finally, the study shows the goals for the new Ellipsometer

have been exceeded in the development of a new robust user friendly operator interface, ease of operation, features and their benefits.

A NOVEL SMALL SCALE WATER SEPARATION INSTRUMENT, WSI

Alan J. Fougere, Ian Mylrea, and Paul Spitteler

D-2 Incorporated along with Stanhope-Seta has developed a new instrument for Small Scale Water Separation determinations consistent with the current ASTM Test Method D3948. The current small scale separometer listed in the method was a test originally introduced in the 1970's has recently been plagued with poor repeatability & reproducibility. The new fully automated sensor and sample handling system that uses a novel detector along with new 5th Edition API Filter materials has been shown to improve consistency of ASTM 3948 results. Results from Filter Test Stand Correlations to WSI readings will be presented. An active ASTM task force completed WSI ruggedness trails earlier this year and data from that program will also be presented.

IN-LINE TURBIDITY/HAZE DETECTION IN REFINED FUELS

Kam Mohajer and Craig McWhorter

In-line turbidity or haze detection is vital for the accurate and efficient monitoring of refined fuels. The real-time data provided reduces the need for manual sampling and can be used to alert remote monitors to off-specification batches prior to transport. This is particularly vital in situations where multiple parties are involved and it is important to determine the source of contamination.

Generally these devices are placed on refinery distribution lines and at pipeline terminals, both incoming and outgoing lines. By doing so, both pipeline and refinery operators are able to ensure the quality of their product prior to receiving and/or distributing. In one case study, a pipeline operator was receiving off-specification batches from a refiner and only discovering the problem at the marketing terminal, nearly 480 kilometers away. These batches had to be trucked back to the refinery at considerable cost. By placing an in-line turbidity/haze meter on the refinery distribution line, and on the main pipeline, operators were able to detect bad batches coming from the refinery and confirm the quality of existing products entering the terminal from upstream on the main pipeline. Data from the turbidity/haze meters is remotely monitored with alarm set points. Off-specification batches are confirmed by site sampling and rerouted to be re-refined. Additional applications would include monitoring jet fuels for water contamination at multiple sites, including dedicated and multi-product pipeline delivery, outgoing lines from the tank farm, and at loading sites for trucks and tank wagons. As turbidity can take the form of water or particulate contamination, these meters can also be used for monitoring fuel filter performance.

SESSION 5A: TESTING (continued)

MAXIMIZING EFFICACY OF FIELD EVALUATIONS OF THERMAL OXIDATIVE STABILITY

George R. Wilson, III, Jill Bramer

The US Army has developed and mobilized a field forward fuel analysis lab, the Petroleum Quality Analysis System - Enhanced (PQAS-E). While the system is capable of evaluating both diesel fuel and jet fuel, the emphasis is on jet fuel because the NATO Single Fuel Forward doctrine stipulates all force projection activities will be conducted with fuel grade F-34 (US JP-8). One critical test for that fuel is the evaluation of Thermal Oxidative Stability by ASTM D3241 (IP 323). This method requires a subjective evaluation of the final results, by visual examination of tube deposits, and that poses a training and validity issue for a system that relies on soldiers and not career laboratory technicians. This paper will consider the potential for using automated heater tube deposit evaluation systems to improve the reliability of the analyses performed by the PQAS-E. First the paper reviews the available rating techniques, their strengths and weaknesses. Then the paper challenges the evaluation systems with a set of marginal heater tubes (i.e. around the failure point) to see how well they perform in identifying potential issues. Finally the paper will review these questions:1) Is the existing visual method sufficient when using temporary technical operators?; 2) Can automated heater tube rating systems be used to augment the performance of the visual system? 3) Should the visual rating method be replaced with an automated system, regardless of standardization level?

A FIT-FOR-PURPOSE SCREENING TOOL BASED ON STATISTICAL MODELING OF FUEL COMPOSITION

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

The high cost and limited availability of emerging alternative fuels is often a major impediment to certification of these fuels as Fit-For-Purpose (FFP) for the U.S. Navy. A method whereby a candidate fuel could be rapidly screened for most of the FFP properties, using a minimal volume (< 1 mL), would overcome this limitation. We have previously reported on our development of a fuel property screening tool for shipboard quality surveillance, based on chemometric modeling of near-infrared (NIR) spectra. While this is a proven viable approach for known (calibrated) fuels, spectral modeling is not practical when applied to fuels that are radically different in composition (uncalibrated), from those used to derive the models. Thus, spectral modeling was deemed impractical as a tool to model properties of alternative fuels and/or blending stocks with unknown compositions. In order to meet this need, we have been investigating algorithmic modeling strategies to elucidate the relationships between composition and critical FFP fuel properties. This has allowed us to develop partial least squares (PLS) models based on gas chromatography-mass spectrometry (GC-MS) data that predict fuel properties more accurately than NIR. More significantly, these models are also capable of predicting FFP properties of uncalibrated alternative fuels. This presentation will describe our development of a FFP screening tool that incorporates both compositional property modeling and the NRL fuel profiler

that provides compound class and carbon number distributions as well as the list of compounds identified in the fuel by the NIST GC-MS library search.

EI/JIG STANDARD 1530 QUALITY ASSURANCE REQUIREMENTS FOR THE MANUFACTURE, STORAGE AND DISTRIBUTION OF AVIATION FUELS TO AIRPORTS

Anja Heckert

A new standard has been published jointly by the Energy Institute and the Joint Inspection Group, which sets out the minimum requirements to be followed to ensure aviation fuel quality and cleanliness, from its point of manufacture through to airports. EI/JIG 1530 is referenced by ICAO Document 9977 Manual on civil aviation jet fuel supply, which has been issued to the 192 member states of ICAO for their implementation. It therefore has a clear global application. EI/JIG 1530 has been drafted by a team of aviation fuel quality specialists from major oil companies, pipeline operator and an international inspection company, with significant technical input from industry stakeholders/specialists worldwide. The key objective in preparing the standard has been to establish for the first time, an industry- agreed minimum level of aviation fuel quality assurance, and good practice recommendations, based on custom and practice that has been established and followed by major fuel suppliers for many decades. The content includes: an overview of quality assurance and traceability; management of change; sampling and testing; requirements for laboratories; manufacturing requirements; use of additives; receipt, batching, certification and release; storage design features and handling procedures; transportation facilities and procedures; requirements for synthetic jet fuel; example certificates

There is an expectation within industry, that the requirements of EI/JIG 1530 will be implemented by all companies/organizations worldwide who are involved in the manufacture, storage or handling of aviation fuel upstream of airports. Future work will include the preparation of materials/tools to facilitate self-assessment by companies/organisations against the requirements of EI/JIG 1530. Feedback on the technical content is welcome.

DLA ENERGY PROCUREMENT, DISTRIBUTION, AND QUALITY OF ALTERNATIVE AVIATION FUELS FOR CERTIFICATION AND APPROVAL

Pamela M. Serino

DLA Energy has procured most all of the alternative aviation fuels for certification and approval within the DOD. This has added up to almost 2million gallons in contract awards including Fischer-Tropsch (FT), Hydroprocessed Esters and Fatty Acids (HEFA), Alcohol to Jet (ATJ) and Direct Sugar to Hydrocarbon (DSH) Fuels. They have been supplied by multiple vendors, from an assortment of locations, made from various feedstocks, and transported thousands of miles.
Although we have been very successful in procuring and shipping these products, it has not come without challenges. DLA Energy was tasked with walking new small business suppliers through the government solicitation process, working as a liaison between the customer requirements and the supplier capabilities, not to mention unforeseen quality issues in handling and shipping of the products from these small-scale production facilities to the end user. But in the end, the DOD

was able to perform all the required testing and certification of military platforms for the use of these alternative aviation fuels and stay in step with the approval of several of these fuels in the commercial aviation fuels specifications.

SESSION 6: ANALYTICAL METHODS

USE OF SCANNING BROOKFIELD VISCOMETRY AS A VISCOSITY EQUIVALENT METHOD FOR JET FUEL FREEZING POINT

Steven Zabarnick, Linda Shafer, Rhonda Cook, and Zachary West

Current jet fuel specifications utilize fuel freezing point and single temperature kinematic viscosity measurements to specify jet fuel low temperature properties. While the specifications have generally allowed safe operation of aircraft worldwide, there is a view in the industry that these test methods do not sufficiently predict the low temperature performance of jet fuel during actual aircraft operations on long duration, high altitude flight (1). Recently, CRC funded a study to explore various improved methods to assess fuel low temperature properties (2). This study recommended the "development and assessment of a suitable low temperature scanning viscometer for jet fuel specification use." In the current work we explore the use of Scanning Brookfield Viscometry (SBV) as a viscosity equivalent method for specifying the low temperature properties of jet fuels. SBV curves of a series of over 40 conventional and alternative jet fuels, and their blends, were measured over the temperature range -40 to -70°C. The "viscosity knee" temperature, i.e, the temperature at which there is a sudden rise in fuel viscosity due to alkane crystallization upon cooling, was identified as a useful viscosity parameter which correlates well with freezing point. SBV measurements are augmented with kinematic viscosity measurements as well as quantitative n-alkane analyses to help elucidate the contribution of the bulk chemical constituents in determining low temperature flowability of jet fuels.

OXIDATION STABILITY OF JET FUEL MODEL MOLECULES EVALUATED BY RAPID SMALL SCALE OXIDATION TESTS

Mickaël Sicard, Jacques Ancelle, Jean Boulicault, Bruno Raepsaet, Frédéric Ser

Jet fuel, besides its fuel role, can be used as a coolant for aircraft subsystems and thus it may be exposed to temperatures above 200 °C. Between 140 and 300 °C, an autoxidation phenomenon occurs due to the presence of 70 ppm of dissolved dioxygen in jet fuel resulting in the formation of oxidized products and solid deposits. The aim of this work is to study the behavior of jet fuel model molecules in order to highlight their oxidation sensitivity and the solid products formed. A rapid small scale oxidation test (RSSOT) is used. Within the RSSOT's test chamber, 5 mL of fuel is combined with oxygen, at 700 kPa, and heated up to 150 °C. This initiates a fast oxidation process. As the fuel oxidizes, it consumes the dioxygen resulting in a pressure drop that is recorded. Different tests are carried out and stopped at various values of the pressure drop. Gaseous and liquid samples are recovered and analyzed by infrared spectroscopy and gas chromatography. In the case of n-dodecane, its consumption is observed up to a pressure drop of

50 %. At the same time, oxidized products are formed among which are alcohols, ketones and carboxylic acids. For higher values of pressure drop, the quantity of alkane does not evolve anymore and some of the products formed disappear. The gas analysis shows that all the dioxygen has been consumed and, surprisingly, reduction reactions occur.

HEAT TRANSFER EVALUATION BY SMALL SCALE TUBE-IN-SHELL SIMULATOR

George R. Wilson, III

Many fuel systems are designed in a manner that heats the fuel. This may be for functional reasons or it may be incidental due to the proximity to the engine. While the technique has been standardized for a few applications, such as ASTM D3241 for jet fuel, it has practical applications for fuels ranging from liquid petroleum gases to bunkers. This paper will review the basics of developing a test strategy based on the fuel in question, illustrate a variety of methods for evaluating the results and discuss the practical applications and limitations of the technique.

ANALYSIS OF PHENOLIC ANTIOXIDANTS IN FUELS BY GAS CHROMOTOGRAPHY MASS SPECTROMETRY

Robert E. Morris, Thomas N. Loegel, Kristina M. Myers and Christopher J. Katilie

Antioxidant additives (AO) are commonly employed in military fuels to mediate autoxidation during storage. Hindered phenols are typically used for this application since they are effective in reducing free-radical chain branching by donation of a hydrogen atom. Antioxidants are typically assayed in fuels by high performance liquid chromatography with electrochemical detection (HPLC-ECD). However, this method is not selective for many of the individual phenolic components of common AO additive packages, and can be difficult and time consuming. While it is possible to extract phenolic antioxidants from fuels with a liquid-liquid extraction, we found this method was subject to numerous interferences, resulting in low reproducibility and unacceptably high detection limits. The goal of this study was to develop a gas chromatography – mass spectrometry (GC-MS) method that provides a direct and accurate quantification of all the common AO components in jet and diesel fuels. We initially developed a single column method that employs a 60 m low polarity column for the separation of AO from the fuel sample matrix. Using GC-MS with selected ion monitoring (GC- MS-SIM), improvements in detection limits and reproducibility were achieved over the liquid- liquid extraction method but co-eluting fuel components interfered with the detection of many of the analytes. To isolate each of the different hindered phenols, a quasi-two dimensional GC configuration was employed through the use of a Deans switch. A primary separation was achieved using low polarity capillary column from which analytes were heart cut and injected onto a more polar capillary column, then sent to a mass spectrometer operating in SIM mode. This GC-MS-SIM heart cut method provides improved detection limits below 300 ppb.

APPLICATION OF MICROBIAL METABOLISM STOICHIOMETRY IN MODELLING BIO-FOULING ASSESSMENT IN GAS TURBINE LIQUID FUELS

Tosin Onabanjo, Giuseppina Di Lorenzo, Eric Goodger and Pericles Pilidis

High reliability, availability and emission compliance are few of the quality requirements and demands in the gas turbine industry. Gas turbine engines are characterized by competitive performance and efficiencies, but often limited by operational and component inefficiencies, one of which is brought about by compromised fuels. These fuels carry unwanted materials such as rust, dust, contaminated air or water droplets harboring microorganisms, of which hydrocarbon-degrading bacteria are of primary concern. The microorganisms exert one or more degradatory effects, particularly, the disappearance of certain hydrocarbon fractions and changes to physical and chemical properties of the fuels. These often result in the accumulation of sludge and initiation of other bioprocesses, such as corrosion with huge cost implications. Previous studies have identified the microorganisms associated with fouling and factors promoting their growth. However, their effects in gas turbine fuels and fuel systems have not necessarily been quantified. Thus, a thorough understanding of the mechanism of bio-fouling in gas turbines is necessary, especially with recent focus on alternative fuels and blends. This work presents an application of fundamental concepts of thermodynamics and bio-energetics in demonstrating and evaluating bio-fouling in gas turbine fuels. Here, the microbial cell is considered as a black box, in which microorganisms utilize hydrocarbon substrates for energy, biosynthesis and cell maintenance. Preliminary analysis on surrogate jet fuel and two other model fuels (BX-F and BX-M) indicate a 15%, 21% and 23% degradation loss of the bio-available fractions respectively and thermodynamically, the biofuel range of fuels resulted in more cell yield than the conventional fuel. This model is considered of prime importance in engineering design decision and analysis of microbial fuel degradation.

SESSION 7: PROPERTIES & EFFECTS

EVIDENCE FOR A LINK BETWEEN FUEL LUBRICITY LOSS AND FORMATION OF SODIUM DEPOSITS

Stephen Cook, Keith Woodhall, and Jacqueline Reid

Sodium salts of carboxylic acids used as corrosion inhibitors have been identified as one component of some internal diesel injector deposits (IDID). Recently, a proportion of US ultra-low sulphur diesel (ULSD) fuels were found, in the field, to exhibit diminished lubricity properties. One hypothesis was that a link existed between these phenomena: Carboxylic acids are frequently used as lubricity improvers in ULSD, should so-treated fuels contact sources of aqueous sodium ions at high pH, formation of sodium soaps and loss of lubricity benefits would be expected. The paper will describe the studies undertaken to evaluate the possible link and provide practical alternative solutions.

IMPACT OF BIODIESEL ON FILTERABILITY AND COLD FLOW PROPERTIES OF DIESEL BX

Roberta Miranda Teixeira, Laila de Castro Cortás, Sérgio Luiz C. Viscardi, and Eduardo H. S. Cavalcanti

Currently, diesel fuel commercialized in Brazil contains 5% of biodiesel. Brazil is one of the largest producers and consumers of biodiesel in the world, with an average annual production of 2.4 billion liters. Biodiesel is produced from different raw materials, but in Brazil, the main ones are soy, animal fat and, recently, cotton. The aim of this present study is to correlate cold flow properties (cloud point, pour point and cold filter plugging point), filterability and composition of biodiesel from different sources. In addition, the impact of these blends was evaluated in mixtures of diesel BX on the same properties. The important application of filterability is verified in the engine systems injection, where this technique can be considered as how much the fuel is clean. Based on the ability of the fuel to pass by a filter (1,6um) without causing pressure elevation, it is directly influenced by the presence of sediments and impurities, which increases the value of filter blocking tendency (FBT) and decreases the life of the filters used, causing obstruction of nozzles and their early wear. The results obtained by gas chromatography, CP, CFPP, PP and filterability shown a important correlation for different blends of biodiesel and BX levels. The major impact was verified on Diesel that shown a filter blocking elevation tendency with increasing the of biodiesel percentual in the blend.

THERMAL OXIDATIVE STRESS OF CONVENTIONAL AND SYNTHETIC FUELS IN A DYNAMIC SYSTEM: IMPACT ON FIT FOR PURPOSE PROPERTIES.

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

With fuel systems providing a greater role in the thermal management of aircraft systems, the fuel is subject to higher temperatures than previously experienced, making it more susceptible to oxidation. In previous IASH papers, we have reported the effect that dynamic stressing has on the formation of hydroperoxides, it's impact on additives and the formation of tertiary oxidation species in the low temperature regime of 140 – 165 °C. However, the effect of dynamic stressing on selected fuel physical properties has not been investigated. This paper will examine the species formed and the impact they have on fuel properties such as water separability and sedimentation. Multiple pass thermal stressing experiments up to 180 °C has demonstrated that "fit for purpose" testing such as water separability (MSEP), particle counting (ISO 4406) and JFTOT have been impacted when subjected to repeated thermal stress. Initial results indicate a reduction of up to 80 °C in the breakpoint temperature of stressed fuel can occur after a residence time of one hour at 180 °C. To complement this, an increase in the particle counts was observed with each stressing event. The behaviour of two fuels processes, viz. hydrotreated and MEROX, gave two differing sedimentation pathways. Interestingly, fuels that have undergone thermal stressing appeared to have thermal memory with the fuel darkening and sedimentation continuing to occur after the thermal process had been completed.

CHARACTERISTICS OF NEAT AND BLENDED HYDROTREATED RENEWABLE DIESEL UNDER STORAGE AND SEAWATER BALLASTING CONDITIONS
Petra Kamenikova, Jinxia Fu, Scott Turn

The US Navy has interest in renewable, drop-in replacement diesel fuels for blending with naval distillate F-76. The shipboard environment and mixed fuel-seawater ballasting practices present unique conditions for preserving fuel quality. F-76 must satisfy specifications identified in MIL-DLT-16884L and this includes measures of storage stability. Two accelerated methods for storage stability determination, ASTM D2274 and ASTM D5304, are identified in the specification and although both were developed for petroleum fuels, their suitability for renewable fuels and fuel blends warrants investigation. In this work, both ASTM accelerated methods are used to evaluate storage stability of hydrotreated renewable diesel (HRD-76), F-76, and HRD-76/F-76 blends. Correspondence of ASTM D2274 and ASTM D5304 and their suitability for evaluating HRD-76 is examined. Results will be compared with long-term storage stability testing according to ASTM D4625. Investigation of potential impacts on fuel-seawater ballasting will be reported. The partitioning behavior of F-76, HRD-76, and their blends in water and seawater (synthetic and fresh) is investigated at various fuel-water ratios under different mixing conditions. C10 to C20 n-alkanes and aromatic compounds are targeted for analysis and can be used to develop surrogates for HRD-76. The transport of inorganic cations (Na+, K+, Mg2+ and Ca2+) from seawater into the fuel is also monitored. In addition, the formation of fuel/water emulsions and dispersions is investigated.

SESSION 8: FUEL PROCESSING

STUDY ON STRONG EBULLATED-BED HYDROTREATING
Liu Jiankun, Yang Tao

Ebullated-bed hydrotreating has made great progress recently because it possesses such features as adaptability to feedstock, almost no reactor pressure drop build-up and reactor, uniform distribution of temperature, on-stream addition and withdrawal of catalyst, long run cycle, flexibility operation, etc. Fushun Research Institute of Petroleum & Petrochemicals (FRIPP) researched and made a greatly technical breakthrough in ebullated-bed technology. Ebullated-bed technology developed by FRIPP has advantages of small catalyst particle and high reactor utilization efficiency. Up to now, FRIPP has redesigned and reestablished ebullated-bed pilot-plant unit with a capacity of 4L/h and accomplished 3000h run cycle. Research of STRONG residue ebullated-bed hydrotreating process The feedstock for test is Iranian atmospheric residue and its properties are that sulfur content is 2.11%; the content of metals (Nickel and Vanadium) is 47.54 μg/g. The diagram of ebullated-bed pilot plant is that a mixture of feedstock and H2 is passed upwardly through a bed of catalyst particles such that the particles are forced into random motion as the liquid and gas flow upwardly through the bed. In the upper portion of reactor, solid catalyst particles are separated from the mixture. The effluent from reactor is fed to high temperature high pressure separator (HHS) in which liquid product is separated from gas. The separated liquid is fed to high temperature low pressure separator (HLS) to flash light component followed by stripping in a stripper, and then fed to product tank. The gas from HHS is fed to low temperature high pressure separator (LHS) to separate light distillate which is fed to product tank

and then is recycled after washed in water-washing column. The reduction of LHSV and increase of reaction temperature advances residue hydrotreating, but the effect of LHSV on reaction result is more evident than temperature. The effect of H2/oil ratio on reaction performance is complex, which involves in the fields of reaction kinetics and hydrodynamics. The removal of impurities ascends gradually to maximum and then descends with the increasing of hydrogen/oil ratio under operation conditions. High removal of impurities is hardly realized in a single reactor for the heavy back-mixing of fluid in reactor, but can be achieved by using multi-reactor in series.

TOOLS AND STRATEGIES FOR THE OPTIMIZATION OF H2S SCAVENGING IN RESIDUAL FUELS: A CASE HISTORY

Stefano Tortora, Giacinto Grande, Alexander Orduz and Carlo Federico Lami

It is well known that on July 1st 2012 a H2S specification was implemented to the revision of the ISO 8217. The limit of 2 mg/Kg in the liquid phase was established for all marine diesel and residual grades. We present here a year-long case history on the application of a H2S scavenger for residual marine fuel in a major European refinery. We can show here how the accurate monitoring as well as the optimization of the dosage rates based on the specific system configuration assure a great cost saving (more than 40% in comparison with the previous treatment) and the required specifications. This significant improvement was possible firstly through the identification of the operative conditions affecting the H2S content in the residual fuel and also the enhanced scavenging action of the additive. Laboratory tests based on real conditions, especially in terms of contact time and mixing degree, allowed us to determine the minimum dosage ratio (scavenger vs. H2S) necessary to reduce the hydrogen sulfide below the specification limit. Thanks to the know-how acquired during our application and the study of the historical data, our technicians applied an additive dosage management based on the process parameters and able to predict the H2S content in the untreated residual fuel. Once optimized, this treatment management had a major impact on the reduction of both the overdosages and the off-specs risk. Moreover, to further improve the prediction accuracy, we developed a mathematical model that was used under the supervision of our experts and gave additional benefits, in terms of efficiency and cost reduction.

SESSION 9: MICROBIOLOGICAL

ADENOSINE TRIPHOSPHATE TESTING – RECENT ADVANCES IN THE DIFFERENTIATION BETWEEN BACTERIAL AND FUNGAL CONTAMINATION AND DETECTION OF DORMANT MICROBES IN FUEL AND FUEL-ASSOCIATED WATER SAMPLES

Frederick J. Passman, PhD, Gulerana Maradukhel, MSc, Michael Merks

Quantification of adenosine triphosphate (ATP) in fuels and fuel-associated waters was first presented at the Technische Akademie Esslingen 6th International Fuels Colloquium in 2007. At the time, two issues limited the overall usefulness of ATP as a test parameter: inability to differentiate between bacteria and fungi and inability to detect dormant microbes. Recent

research has addressed both of these issues. This paper presents protocols for detecting dormant microbes – identified as microbes that are not metabolically active in the sampled fluid, but which can become active under appropriate conditions – and for differentiating fungi from bacteria. The newly developed protocols achieve >90% detection of bacterial endospores in fuels and fuel-associated water. They also provide >90% differentiation between bacterial and fungal contaminants in these fluids.

BIYOTRAP AS A FRONT-END FOR NUMEROUS BIOTECHNOLOGIES

Mark L. Wolfenden, Muhammedin Deliorman, and Recep Avci

It would be highly desirable to detect the early stage of the bacterial contamination of a fluid so that effective preventative measures could be taken before problems reached serious levels. Most of the conventional detection techniques are highly effective provided that the concentration of the contaminating bacteria is above a certain limit, typically ~103 cells/mL or higher. However, when bacteria have reached this level of contamination it may already be too late to initiate counter measures to prevent the spread of the problem or to prevent damage. It would be desirable for contamination to be detected at a much lower level, something like 10 cells/mL level or lower. Most of the conventional tests for detecting organisms are ineffective at this level, so it is necessary to concentrate the organisms in an effective and efficient way within a relatively short period of time (<1 hr). Most of the existing methods are based on size exclusion techniques involving complicated and costly filtration technologies. These approaches usually face serious problems involving filter clogging and issues collecting bacteria from filter surfaces. Here we report a very practical and effective method of capturing bacteria which is based on short-range electrostatic interactions on a 3-D network of activated glass fibers. This method offers great potential for the enrichment of bacteria from dilute solutions as a front end technology to be applied before other techniques are used to search for bacteria, as shown in Fig.1. below. We will present the chemistry and application of this technology in contaminated fuels and aqueous environments.

FUEL MICROBIOLOGY TEST METHODS – CAN WE REALLY DETERMINE PRECISION AND BIAS?

Frederick J. Passman, PhD

There are several challenges associated with the use of microbiological parameters as fuel quality criteria. Microbes proliferate only where there is sufficient free-water to support metabolic activity. Consequently, microbes are most often detected in fuel-associated water rather than fuel itself. Samples well suited for testing other fuel quality parameters are generally inappropriate for microbiological examination. Distribution of microbes is typically quite heterogeneous. Consequently, variability among replicate samples from the same source can be sufficient to lead to different conclusions regarding the need for corrective action. Notwithstanding these challenges, microbiological test data provide useful information about microbial contamination in fuels and fuel systems. Understanding the factors contributing to data variability and bias provides users for these data with the perspective needed to interpret them

objectively and accurately. In 2012, ASTM approved D7847 Guide for Interlaboratory Studies for Microbiological Test Methods. This paper reviews the primary issues addressed by D7847.

A NOVEL APPROACH TO DEVELOP A HYDROCARBON-BASED ATP- BASED STANDARD FOR USE IN RAPID ASSAY BIOLUMINESCENCE TESTING

Edward English

Testing for microorganisms in petroleum-based fuels has been traditionally performed using some form of nutrient based growth media. Generally, this type of test method is compatible with water samples. There are some test methods that can analyze for microorganisms in both aqueous and petroleum-based matrices. In the past decade new test methods have been introduced that rapidly identify the presence of microorganisms indirectly by applying alternate technologies such as bioluminescence assay. Generally, instrument response or calibration of the newer detection technologies is performed indirectly by measuring a known quantity of the analyte of interest. For example, the sodium salt of adenosine triphosphate (ATP) in an aqueous media. This paper discusses the worked performed to support the Proof of Concept for a hydrocarbon-based standard that contains cellular and extracellular forms of adenosine triphosphate (ATP) that can be used as a tool on a limited basis with bioluminescence assay.

INTERLABORATORY STUDIES OF A THIXOTROPIC GEL CULTURE METHOD FOR FIELD AND LABORATORY TESTING FOR MICROBIOLOGICAL CONTAMINATION IN FUELS

Graham C. Hill, Derek J. Collins & Andrew Ryan

The fuels industry has seen an increasing focus on use of regular microbiological testing to establish whether microbiological growth is occurring in distribution facilities and end user tanks and thus provide assurances that fuel is free of microbiological contamination. A number of laboratory and field methods are available, reliant on both conventional culturing techniques and non-conventional assessment methods. However, only limited studies have been conducted to establish the reliability of these methods. This presentation will discuss some of the challenges in developing and conducting an Inter-Laboratory Study (ILS) to establish repeatability and reproducibility of microbiological test methods for fuels. It will describe the approach taken and results obtained in an ILS of a thixotropic gel culture method which is widely used in the petroleum industry both in the field and in laboratories. The ILS was undertaken with a view to publishing the technique as a new IP standard method.

A COMPARISON OF THREE DIFFERENT ACTIVES AS FUEL MICROBICIDES IN REGARDS OF THEIR BACTERICIDAL AND FUNGICIDAL EFFECT

Wolfgang Siegert and Quyen Ziegann

The microbial contamination in diesel fuel has become a problem with a huge impact. And it is spreading. The problem has been well-known for over sixty years, when the first fuel contamination case was recorded. Until recently the only effects were on vehicles with a long

standstill and storage tanks with low turnover. By the introduction of bio- diesel („FAME“) in diesel and heating oil this issue has gotten a new dimension and new cases are recorded on a daily basis. Different fuel mirobicides are used to stop this problem but how effective is a chemical treatment against different types of microorganism? Three biocide actives have been tested with the standard ASTM E-1259-05 test method. The actives are: A) 3,3'-Methylenebis[5-methyloxazolidine] (MBO); B) mixture of 5-chloro-2-methyl-3-(2H)-isothiazolone (CMI)+2-methyl-3-(2H)- isothiazolone (CMI/ MI); C) mixture of 4-(2-nitrobutyl)morpholine and 4,4'-(2-ethyl-2- nitrotrimethylene)-dimorpholine. The test has been done with the lowest, middle and highest use concentration recommended by the manufacturer. Test results show excellent efficacy of MBO against all tested microorganism types such as bacteria, yeast and mould. The active MBO shows the fastest action at all use concentrations in both in the water and in the fuel phase. The test results show that a quick kill effect and also the long-term protection can be provided with MBO.

TRANSCRIPTIONAL RESPONSE OF BACTERIA TO JET FUEL

Oscar N Ruiz

Microbial contamination of jet fuels is a known problem. Extensive microbial growth and biofilm formation can lead to costly and disruptive damages to fuel systems and aircraft hardware which can severely affect mission performance. The military needs to be prepared against microbiological contamination of fuels. In order to prevent and mitigate microbial contamination of fuels, better understanding of the genetic mechanisms that lead to microbial colonization and proliferation in fuels is required. Most studies have been dedicated to identify microorganisms present in a given fuel sample. More in-depth studies are required to understand why and how these microbes can proliferate in aviation fuels, and the extent of the damage they can produce. Here we characterize the regulation of metabolic genes common to bacteria that affect conventional and alternative fuels. This information can be used to develop more effective and targeted microbial mitigation strategies. In order to expedite the identification of valuable target genes, we applied cutting-edge metagenomics, transcriptomics, and bioinformatics approaches to study growth and gene expression patterns of relevant bacteria in conventional and alternative fuels.

SESSION 10: ANALYTICAL METHODS & EFFECTS OF ADDITIVES

EMULSION FORMING TENDENCIES OF CORROSION INHIBITOR ADDITIVES

Enrico A. Lodrigueza

Phillips 66 has remediated product terminal gasoline tank bottoms that consisted of a severe white, milky emulsion. Extensive analysis showed the emulsion was formed from a reaction between caustic and corrosion inhibitor additive. A modified ASTM D 1094 water reaction test method was used to evaluate the emulsion forming tendency of corrosion inhibitor additives. The haze, the amount of emulsion, and changes in the volume of the aqueous layer over time were

observed. Eight commercially available conventional and synthetic corrosion inhibitor additives were evaluated. One class of synthetics produced negligible amounts of emulsion and exhibited the best water separation.

SULFUR DEPOSIT FORMATION DURING HIGH TEMPERATURE THERMAL STRESSING OF JET FUEL

Paul Rawson and Sylvester Abanteriba

Aviation fuel thermal stability is defined by its resistance to deposit formation while undergoing thermal stress. Thermal deposits have normally been characterized visually or when quantified, as a total deposit mass or specifically related to carbon mass. It has been observed that some fuels, specifically MEROX treated, tend to form high levels of sulfur containing deposits, some times of greater mass of total sulfur than carbon. This work describes sulfur deposit formation quantified by total sulfur analysis using a LECO CS-244 from jet fuels over a range of temperatures (300 – 400ºC) and flow conditions (0.5 – 2 ml/minute) in a single pass thermal stability rig. It was observed that sulfur deposit mass increased with temperature and decreased with increasing flow rate. Sulfur deposition rate also decreased with total mass of fuel stressed suggesting influences from changes in deposit thermal conductivity on the reaction vessel surface.

FIELD EVALUATION OF PARTICLE COUNTING TECHNOLOGY IN THE US MILITARY FUEL SUPPLY CHAIN

Pamela M. Serino

Aviation turbine fuel contaminated with particulates and water is a serious quality concern for US DLA Energy and the military services. The current test methods (ASTM D 2276, and ASTM D 4176) for determining particulate matter is inadequate, subjective, and have acknowledged limitations in providing reliable data in determining particulate contamination. In recent years, the UK Energy Institute published the standards EI 1570 and EI 1598 for monitoring free water and/or particulate matter in aviation fuel, and ASTM D7619 was also published utilizing laser obscuration sensor technology for same purpose. Currently DEF STAN 91-91, MIL-DTL-83133 (JP-8) and upcoming MIL-DTL-5624 (JP-5) include a report only requirement for particle counting using IP 564, IP 565, or IP 577. Recently there were few lab and rig scale programs in US for evaluating the laser obscuration particle counting instruments in fuel. US DLA Energy led/conducted a first field evaluation program of particle counter technology for fuel contamination monitoring with off-the-shelf commercially available particle counters. The program monitored fuel quality over defined periods of time at predetermined points within the fixed and mobile infrastructure used to store and distribute aviation turbine fuel throughout the US military fuel supply system. Since laser obscuration technology based particle counters are unable to distinguish between free water and sediment contamination, resolver and isopropyl alcohol were also tested with the particle counter instruments to try to overcome the technology limitation.

JOHN BACHA STUDENT AWARD PAPER: TOWARDS EFFECTIVE FUEL DEHYDRATING ICING INHIBITORS
Sonia L. Repetto, Norman M. Ratcliffe, Ben De Lacy-Costello and Joseph K.-W. Lam

Dissolved water is a normal component of jet fuel which is vapourised during combustion; however, free water is a contaminant that can starve engines, freeze to form ice crystals capable of blocking fuel feeds, support microbial growth, and contribute towards corrosion. Jet fuel may be protected from the potentially hazardous effects of free-water using biocides and icing/corrosion inhibitors. This investigation seeks to identify novel chemical approaches to the dual management of both water contamination and ice formation in jet fuel. The strategy of using organic dehydrating agents remains relatively neglected, perhaps because of the complexity of the physical organic chemistry involved in developing and refining these systems. However, organic molecules with well characterised dehydrating properties - such as ortho esters, acetals, hemiacetals, ketals, hemiketals – present themselves as ideal candidates for development and optimisation. This paper describes our systematic approach towards the development of kinetically fast, selective organic jet fuel additives capable of converting water into combustible products which also possess ice inhibitor characteristics. We anticipate that this class of Fuel Dehydrating Icing Inhibitors (FDII's) represents a novel approach towards protecting jet fuel against the effects of water contamination.

POSTER SESSION

TOOLS AND STRATEGIES FOR THE OPTIMIZATION OF H2S SCAVENGING IN RESIDUAL FUELS: A CASE HISTORY
Stefano Tortora, Giacinto Grande, Alexander Orduz and Carlo Federico Lami

Scavenging H2S from petroleum products may be easy but doing it efficiently is much more challenging. Too often some important aspects are overlooked causing extra costs in the best case and off-specs in the worst ones. Through the example of a case history we want here to show the impact that the proper approach in the treatment management can have on dosage rates and therefore costs. It has to be concrete but also creative in the development of specific solutions or new tools able to make the difference in the results achievable.

TOWARDS PREDICTIVE MAINTENANCE IN GAS TURBINES- SIMULATION AND ANALYSIS OF FUEL DETERIORATION
Tosin Onabanjo, Giuseppina di Lorenzo and Eric Goodger

CHROMATOGRAPHIC ANALYSES OF ALKYLDIHYDROFURANONES IN THERMALLY OXIDISED ALGAE-DERIVED JET FUEL
Renee L. Webster, David J. Evans, Blagoj S. Mitrevski and Philip J. Marriott

Modern jet aircraft use fuel for cooling avionics and lubricant systems, exposing it to temperatures > 150 °C. This leads to oxidation of the fuel and formation of heteroatomic species

which are deleterious to fuel properties and aircraft operation. Oxidised species are implicated in formation of insoluble particulates and gums (Fig. 1), causing poor engine performance, increased maintenance, and potential engine failure. The mechanism of formation of species resulting from three or more oxidation steps (tertiary oxidation compounds) is largely unknown, due to difficulties in identifying these compounds in the highly complex fuel matrix. One class of largely unexplored tertiary oxidation products is alkyldihydrofuranones (furanones), recently shown to form in fuels in shorter times (<1 hr) and at lower temperatures (140 °C) than previously observed.

RAMP-CHECK, A HANDHELD INSTRUMENT FOR QUANTITATIVE ASSESSMENT OF FUEL PHYSICAL PROPERTIES IN THE FIELD
Alan J. Fougere

HIGH MOLECULAR WEIGHT POLYSIOBUTYLENE DIESEL ENGINE COMBUSTION TECHNOLOGY IMPROVEMENT
David R. Forester

Diesel engines are a primary source of power for transportation and in some parts of the world for the production of electric power. They are currently about 40% efficient in converting a fuel's energy to work. Diesel engines are also major emitters of NOx and PM exhaust emissions. Leaner overall combustion could significantly increase diesel engine efficiency and reduce harmful exhaust emissions. Ultra-high molecular weight polyisobutylene makes diesel engines run leaner by modifying the physical properties of the fuel to give it viscoelastic behavior.

CHARACTERISTICS OF NEAT AND BLENDED HYDROTREATED RENEWABLE DIESEL UNDER STORAGE AND SEAWATER BALLASTING CONDITIONS
Jinxia Fu, Petra Kamenikova, and Scott Turn

The development and utilization of alternative fuels have become an ambitious energy goal for industrialized countries striving to decrease reliance on foreign sources of oil. The US military is the largest single energy consumer in America1. In keeping with the five energy targets announced by Secretary of the Navy Ray Mabus in October, 2009, the US Navy has interest in renewable, drop-in, alternative diesel fuels for blending with NATO F-76. An alternative fuel of particular interest is hydrotreated renewable diesel derived from algae (HRD-76), and the US Navy has identified a blend of 50% F- 76 and 50% HRD-76 to meet the alternative fuel requirements. Combustion system assessment test results indicate that a 50/50 blend performs satisfactorily.2 However, the shipboard environment and mixed fuel-seawater ballasting practices present unique conditions for preserving fuel quality. The 50/50 blend must satisfy specifications identified in MIL-DLT-16884L for F-76, and this includes measures of storage stability, the current objective.

IMPACT OF BIODIESEL ON FILTERABILITY AND COLD FLOW PROPERTIES OF DIESEL BX

Roberta Miranda Teixeira, Laila de Castro Cortás, Sérgio Luiz C. Viscardi and Eduardo H.S. Cavalcanti

Currently, diesel fuel commercialized in Brazil contains 5% of biodiesel. Brazil is one of the largest producers and consumers of biodiesel in the world, with an average annual production of 2.4 billion liters. Biodiesel is produced from different raw materials, but in Brazil, the main ones are soy, animal fat and, recently, cotton. The aim of this present study is to correlate cold flow properties (cloud point, pour point and cold filter plugging point), filterability and composition of biodiesel from different sources. In addition, the impact of these blends was evaluated in mixtures of diesel BX on the same properties. The important application of filterability is verified in the engine systems injection, where this technique can be considered as how much the fuel is clean. Based on the ability of the fuel to pass by a filter (1,6um) without causing pressure elevation, it is directly influenced by the presence of sediments and impurities, which increases the value of filter blocking tendency (FBT) and decreases the life of the filters used, causing obstruction of nozzles and their early wear. The results obtained by gas chromatography, CP, CFPP, PP and filterability shown a important correlation for different blends of biodiesel and BX levels. The major impact was verified on Diesel that shown a filter blocking elevation tendency with increasing of biodiesel percentual in the blend.

THE INFLUENCE OF SURFACE AREA TO VOLUME RATIO ON LONG-TERM STORAGE OF JET FUEL, A FIELD STUDY

Yalfal Siyum, Moshe Rabaev, Udi Akiva, Noam Brown, Eytan Geissmann, Rephael Fass, Joseph Geva, Josefa Ben Asher

Though it is generally known that a surface area to volume ratio (SA/V ratio) has a bearing on long-term storage stability of jet fuel, little real field data exists on this subject. In this field study, the stability of jet fuel stored for 2 to 10 years in 30 liter, 10m3, 300m3, 30,000m3 tanks and in a 150 km section of 16" pipeline, has been evaluated in relation to impact of SA/V ratio. The tests performed included the general specification requirements, long-term storage evaluation tests and microbiological tests. The data suggests that straight run jet fuel may be safely stored under good housekeeping conditions for ten years in carbon steel or stainless steel made storage tanks, having a SA/V ratio less than 3. Contrary to that, storage of straight run jet fuel, for only two years, in an underground 150 km section of 16" carbon steel pipeline, having SA/V ratio of 10, went off spec regarding existing gum. The storage conditions in this pipeline supported accumulation of water and rust particles in topographically low sampling points that could have contributed to the deterioration process. In small aluminum made tanks bearing SA/V ratio higher than 20, JFTOT deteriorated within several months of storage. This study sets a basis for an initiative to collect more historical data on this subject from various sources. A broader data base will enable to determine a solid numeric indicator to be used for decision making, regarding strategic storage of jet fuel in remote locations, based on volume, structure, construction materials and design considerations.

LONG -TERM STORAGE OF B0-B20 BLENDS – A CHEMICAL AND A MICROBIOLOGICAL STUDY

Noam Brown, Joseph Geva, Rephael Fass, Ella Fastovsky, Eytan Geissmann, Udi Akiva, Moshe Rabaev, Yalfal Siyum and Josefa Ben Asher

The Latest Standard EN 590 stipulates inclusion of up to 7% of Fatty Methyl Esters (FAME) in automotive diesel fuel. FAME may consist of unsaturated fatty acids, which are prone to auto and microbial oxidation by exposure to air and water. Both can influence the quality of the blends during long term storage. A chemical study was intended to assess whether FAME-diesel blends (B0, B5 and B20) remain stable during long-term storage, with and without additives. Three different additives were assessed: a package of biocide with a stabilizer additive, meeting the requirements of MIL-S-53021 (A), a FAME-specific antioxidant (B) and a mixture of A+B. Sets of blends and additives were stored in sealed standard drums. The storage stability of the mixtures was assessed by EN 15751 tests. The results suggest that B5 and B20 remain stable for more than 42 months, when treated with a mixture of additives A+B. In a separate microbial study, the same blends and additives were stored for one year, under conditions favoring the proliferation of hydrocarbon utilizing microorganisms. The results suggest that FAMEdiesel blends do not support excess microbial growth, as compared to neat diesel fuel under the experimental conditions. It was found that these blends may be stored for one year without additives. Contrary to that, the acidity of B-20 blend with additive (B), increased significantly, as measured following one year of storage. This increase was accompanied by excess fungal growth.

BYOTRAP AS A FRONT-END FOR BIOTECH SENSOR PLATFORMS

Mark Wolfenden, Muhammedin Deliorman and Recep Avci

Bacterial contamination is a problem in many fields including fuel contamination, food borne illness and hospital infection. Contamination is often below detectable limits when it becomes an issue, hence sample concentration is a crucial step to improve and speed up the detection of bacterial pathogens. Bacteria detection lower limits are at ~1000 cells/mL, by the time the microbes can be detected, it is often too late to use counter measures. This technology targets concentrating bacteria to levels where detection methods are reliable and removal of bacteria without the need for size exclusion.

THE EFFECT OF COLD SOAK FILTRATION OF B100 ON SUBSEQUENT COLD FLOW IMPROVER RESPONSE IN B100/ULSD FUEL BLENDS

J. Andrew Waynick

Four current generation cold flow improvers were evaluated at 500 ppm(wt) in three B20 diesel fuel blends. The B20 diesel fuel blends were made by blending a biodiesel-free summer grade ULSD and an ASTM D6751-compliant B100 derived from used cooking oil. The first B20 was made using the B100 as received. The second B20 was made using the B100 after processing by a cold soak filtration process as described in ASTM D6751-10 annex, now ASTM D7501. The third B20 was made using another portion of the B100 similarly cold soaked but filtered cold

after being removed from the cold soak chamber. The resulting three B20 fuels were evaluated with no cold flow improver additive as well as with 500 ppm(wt) of each of the four selected cold flow improver additives. Cold flow tests included Cloud Point, Pour Point, and Cold Filter Plugging Point. Also, FAME Speciation by EN 14103 was performed on two of the B100's. Results indicated that both B100 cold soak filtration procedures failed to provide any significant improvement in the cold flow properties of the additive-free B20 blends as well as the additized B20 blends. FAME speciation showed that even after the cold soak/cold filtration (with a visibly significant portion of the original B100 still solid and not part of the filtrate) the composition of the filtered B100 had not significantly changed relative to the original B100. These results suggest that efforts to improve the cold flow properties of B100 by ordinary fractional crystallization are likely to not be successful beyond imparting compliance with the D7501 requirement of D6751.

OPTIMIZING FATTY ACID DISTRIBUTIONS FROM TEN SHEWANELLA SPP. FOR BIOFUEL PRODUCTION

Emily R. Petersen, Lisa A Fitzgerald, Robert E. Morris, Kristina M. Myers, Jeffrey A. Cramer, Anthony P. Malanoski and Justin C. Biffinger

ORGANOMETALIC NANODISPERSIONS USED AS A COMBUSTION MODIFIER FOR LIGHT HEATING OIL AND AS A SOOT OXIDATION CATALYST ON DIESEL PARTICULATE FILTERS

Michal Wojtasik and Grazyna Zak

Appling the appropriate synthesis methods and some chosen dispersants stable nanosuspensions of iron, potassium and cobalt compounds in organic solvents were obtained. Above mentioned substances (catalysts) improve combustion efficiency of soot, which is generated in diesel fuel and light heating oil combustion process.

STABILITY COMPARISON OF GTL DIESEL/FAME BLENDS AND EN590 DIESEL /FAME BLENDS

Celeste Wilken, Stefan de Goede, Piet Roets, Chris Woolard and Adrian Velaers

CHARACTERIZATION OF SYNTHETIC GAS-TO-LIQUID JET FUEL BLENDS: HYDROCARBON CHAIN LENGTH
EFFECT ON FUEL PROPERTIES & ELASTOMER COMPATIBILITY

Elfatih E. Elmalik, Samah Warrag, Moiz Hafis, Nimir O. Elbashir

Our research objective is to create a model that can predict the properties of a given blend of synthetic fuel formulated from paraffinic and aromatic building blocks- utilizing experimental data, statistical analysis, visualization programs and specified industry standards for jet fuels. This model can then be used to narrow down the search for synthetic jet fuels that fall within aviation industry standard limits. Also, the effect of mono-aromatics (up to 25% v/v) on all the

properties was explored– with a focus on seal swell. As a predictive tool, an Artificial Neural Network (ANN) was developed using the data generated; it proved to be able to accurately predict the property values for any combination of hydro-carbons. Furthermore, a novel visualization technique was developed for 2-D and 3-D interpretation of the results and to identify fuels' composition as per ASTM D-1655 and D-7566 properties limits.

DEVELOPMENT OF AN ADVANCED COMBUSTION RESEARCH FACILITY FOR FUELS, EMISSIONS AND COMBUSTOR OPERABILITY STUDIES

Scott Stouffer, Ray Townsend, Mark Laber, Jerry Grieselhuber, Matthew J. DeWitt, Jacob Diemer, Harold Day, Richard Zierhing, Edwin Corporan and Dale Shouse

Design and optimization of advanced gas turbine engines requires detailed understanding of combustion processes and how these are affected by fuel chemical and physical properties, combustor operating conditions, and system configuration. Impact of fuel chemistry on combustor performance is of interest to identify critical properties for efficient combustion/low emissions and guidance on suitability of alternative fuels. Improved understanding of fuel impacts on combustion performance, ignition, stability and emission production as a function of pressure is of interest. A versatile research facility has been developed to investigate impact of fuel properties, combustor configuration and operating conditions on combustion behavior.

INVESTIGATION OF COMBUSTION AND EMISSIONS PERFORMANCE OF ALTERNATIVE AND CONVENTIONAL FUELS AT THE LIMITS OF THE JET FUEL SPECIFICATION

Edwin Corporan, Tim Edwards, Matthew J. DeWitt, Christopher Klingshirn, David Anneken, Linda Shafer and Andrew Caswell

The impact of fuels with significantly different physical, chemical and ignition properties on the combustion performance and emissions of a T63 turboshaft engine were investigated. The engine was operated at several power settings with experimental fuels, alternative fuel blends, and fuels at or near the maximum and minimum limits of the jet fuel specification for aromatics, sulfur, energy content and density. Combustion temperatures within the primary zone, and soot deposition on the internal combustor walls during extended operation with fuels of different aromatic content was also investigated. The test fuels, derived from conventional and alternative (natural gas, coal and cellulosic) feedstocks, consisted of a wide range of centane numbers and indices. Test results show that the engine operated adequately with the fuels tested, with no significant impacts on combustion performance. Assessment of fuel ignition quality showed minimal correlation between the fuel cetane numbers and engine combustion and fuel conversion (thermal) efficiencies. As expected, non-volatile particulate matter (PM) (i.e., soot) emissions were lower with fuels with reduced aromatic (higher hydrogen) content. However, several fuels with similar hydrogen content yielded significantly different soot emissions, which suggests that the propensity of a fuel to form soot is not only influenced by the corresponding hydrogen content but also by the chemical structure of its components. Visual inspection of the combustor showed that soot deposits decreased with lower aromatic fuels, which suggests potentially reduced engine maintenance, decreased deposition on fuel nozzles (promoting consistent long

term performance), and prolonged engine life with the use of low aromatic fuels. Other than the anticipated higher sulfur oxides emissions with a high sulfur fuel, fuel composition primarily impacted gaseous emissions at engine idle. The largest difference in emissions was observed between a highly cycloparaffinic fuel and a C10 paraffinic fuel, for which up to 30% and 60% less CO and unburned hydrocarbon emissions, respectively, were observed for the lower molecular weight paraffinic fuel. The C10 fuel produced the highest combustion efficiency of all fuels tested (~2 percentage points higher at idle than the baseline JP-8), likely due to its favorable physical properties for combustion. Overall, fuels at the low and high end of the specification for energy content and density produced adequate engine performance, which suggest that it may be possible to relax these requirements to expand the jet fuel specification. This will increase the pool of suitable aviation fuels, which may lead to reduced fuel costs. Obviously, all other aspects of aircraft operation (e.g. range, compatibility, etc.) must be assessed before serious consideration is given to expanding the jet fuel specification.