

# **12<sup>TH</sup> INTERNATIONAL CONFERENCE ON STABILITY, HANDLING AND USE OF LIQUID FUELS**

**Sarasota, Florida  
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## **Abstract Summaries**

### **SESSION 1: RENEWABLE FUELS AND CARBON NEUTRALITY**

#### **THE NEED FOR SUSTAINABLE LIQUID FUEL AND THE PROMISE OF ADVANCED BIOFUELS**

*Don Scott*

Liquid fuels are profoundly important to our society. Liquid fuels are the densest, safest, and most economical way to store energy for a myriad of uses. We rely on liquid fuel to harvest and distribute food. We rely on liquid fuels to transport goods and people. We rely on liquid fuels for emergency vehicles and backup electrical power as just a few examples of its importance. Fossil fuels and petroleum, in particular, are now criticized for greenhouse gas (GHG) emissions and dwindling reserves of crude oil. Sustainability is a measured balance of environmental, economic, and social factors. Our growing global population and current standard of living cannot be sustained without liquid fuel. The challenge faced by the liquid fuels industry is to manage environmental impacts and leverage existing reserves in ways that make the liquid fuels industry sustainable. Major oil consuming nations have already enacted policies that relegate a small percentage of their liquid fuels market to renewable fuels. These policies require renewable fuels to meet specific GHG reductions and often impose additional sustainability requirements. The renewable fuels with the greatest sustainability benefits are being dubbed Advanced Biofuels. This report will detail how the sustainability of Advanced Biofuels is measured and how they can improve the sustainability of the larger liquid fuels industry.

#### **RENEWABLE FUELS: DLA ENERGY GOALS, INITIATIVES AND CHALLENGES**

*Daniel Baniszewski*

As we move through the certification and testing of a variety of alternative fuels, we need to look at the next steps and challenges associated with procuring and using operational quantities of these fuels. The United States military services have announced aggressive goals for the operational use of alternative fuels and DLA Energy will be responsible for procuring them. To support this effort DLA Energy has established many partnerships with commercial industry and other government agencies; particularly the Air Transport Association (ATA), United States Department of Agriculture (USDA) and the Department of Energy (DOE). By leveraging these partnerships DLA Energy has become involved in multiple regional projects designed to facilitate the commercialization of alternative fuels. The major projects DLA Energy currently supports are the Green Initiative for Fuels Transition Pacific (GIFTPAC) and Farm to Fly. During the course of our involvement with these and previous initiatives, DLA Energy has

become aware of many challenges facing the commercialization of alternative fuels. These include supplier concerns such as guaranteed off take agreements, long term contracts and financing; logistical concerns pertaining to fuel specification blending requirements; and environmental considerations relating to lifecycle greenhouse gas emissions, water use, land use and particulate emissions.

## **OVERVIEW OF U.S. NAVY'S SHIP RENEWABLE FUELS EVALUATION**

*Dr. Ryan Turgeon1, Sherry Williams, Richard Kamin, Richard Leung and Dr. Geoffrey Eldridge*

The United States Navy has been evaluating non-petroleum sourced alternative fuels for use as a military shipboard diesel fuel replacement. The Navy requires that any alternative sourced fuels be drop-in replacements that require no modification to existing propulsion systems. Various fuels have been tested including neat alternative and 50/50 blends of alternative/petroleum fuel. Laboratory testing of chemical and physical properties performed on each fuel showed similar or improved properties when compared to petroleum sourced fuels. Performance testing, to include fuel handling and engine testing, has been conducted in marine diesel and marine gas turbine engines. Shipboard demonstration using a 50% algae sourced fuel was conducted aboard two tactical boats. This paper will present the current status and results of the US Navy's program to evaluate alternative sourced diesel fuels.

## **A REVIEW OF SYNTHETIC FUEL DEVELOPMENT FOR USE IN AVIATION**

*Dr. Clifford A. Moses and Stanford P. Seto*

It started with a single request from the Sasol Fuels Technology, Sasolburg South Africa, to approve for use as a blend stock the Iso-Paraffinic Kerosene stream from their synthetic fuel refinery in Secunda, South Africa. The IPK approved would be used to extend the Sasol Natref Refinery petroleum sourced Jet A-1 fuel. This was in 1996. From tiny acorns.....This paper explores what happens when a staid and rigid industry, steeped in a deep and rich history (about 50 years) of producing jet fuel from bulk petroleum bestirs itself to look at something new – Fuel from Synthetic Feedstock! Where has that first hesitant step brought us? What are the sidebars to this story? The Lessons Learned? What...What does the future hold ?? The challenges and the potential payoffs! Well, Maybe just the Challenges....!

## **ALTERNATIVE AVIATION FUELS – PROGRESS AND PLANS**

*Tim Edwards, Kristin Lewis, and Nathan Brown*

The aviation alternative fuel effort is relatively young compared to its ground transportation counterparts but has already seen significant success. Notably, since its inception in 2006/2007, the alternative fuel program has seen a generic Fischer-Tropsch Synthetic Paraffinic Kerosene (SPK) fuel blend approved in ASTM D7566 in 2009. The rapid pace of this approval was due to the cooperation and collaboration of all parts of the aviation enterprise through the FAA-chartered Commercial Aviation Alternative Fuel Initiative (CAAFI), which includes representatives from fuel producers, aviation equipment manufacturers, airlines, airports,

pipeline companies, and military and civilian government organizations. This paper will summarize the Fischer-Tropsch SPK certification effort (and the development and codification of the certification process in ASTM D4054), as well as discuss current certification efforts. Notably the aviation biofuel Hydroprocessed Esters & Fatty Acids (HEFA, aka HRJ and bio-SPK) was approved in 2011. Other fuel processing pathways are under investigation, including various routes to full-synthetic fuels. The paper will also describe environmental studies of the various fuels, as well as discuss various ongoing joint ventures for early fuel production.

## **SYNERGIES BETWEEN RENEWABLE KEROSENE AND FISCHER-TROPSCH SYNTHETIC PARAFFINIC KEROSENE (FT-SPK)**

*Mariam Ajam and Carl L Viljoen*

Fossil-derived fuels have been the source of transportation energy for many decades, but with the increase in fuel prices, environmental concerns and government regulations, the interest in alternative fuels has escalated. The future of the aviation industry, including that of the rest of the transportation industry, will inevitably be driven to the use of sustainable renewable fuels in increasing quantities. This drive is based on the carbon footprint of the aviation industry and the critical need to slow down the growth rate of greenhouse gas (GHG) emissions. Fuel producers have a mandate to explore, develop, and demonstrate future renewable fuel technology options that will ensure sustainability over the long term. The aviation industry's experience with alternative jet fuel has mainly been focused on Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK). FT-SPK derived from coal, natural gas or biomass is now generically approved for commercial use as a blend component with crude-derived jet fuel across the world. This approval became effective in September 2009 with the publication of ASTM D7566. The "greening" of FT-SPK and/or crude-derived jet fuel is a critical action that could become mandatory in future, when a minimum proportion of renewable carbon atoms in the fuel may be required by legislation. Synergies between Gas-to-Liquid (GTL)-derived SPK and hydroprocessed renewable jet (HRJ) fuel, or other renewable jet fuel compounds, could potentially exist. This paper summarises the technical feasibility of a FT-SPK with enough renewable carbon content such that it will be acceptable from a "green" perspective. Property analysis of the blends is reported according to the D7566 specification with special emphasis on thermal oxidative stability.

## **BIOMASS TO LIQUID FUELS FROM NON-FOOD SOURCES – LIFE CYCLE ASSESSMENT WITH COMPARISON TO OTHER ALTERNATIVE FUELS AND PROCESSES**

*Robert L. Freerks, Ph.D.*

As shown by the life cycle assessment study conducted by MIT for CAAFI/PARTNER, there is an extremely wide range of carbon intensity values for SPK jet fuels depending on feedstock, processing and indirect land use change issues associated with the feedstock production. Rentech is developing technology to produce SPK jet fuel with essentially zero to negative carbon intensity using feedstocks that do not compete with food production and have no iLUC issues. Utilizing advanced gasification/Fischer-Tropsch/Heat Recovery/Upgrading technologies, Rentech can produce jet fuel blend components (SPK jet fuel) with exceptionally low carbon

intensity. The Rentech projects under development utilize wood biomass as the primary feedstock where much or all of the biomass is derived from forest residuals from harvesting timber, underutilized or unmerchantable timber or by-product residuals from primary wood processing into lumber and engineered wood products. In some cases the waste from these processes is 90% of the wood delivered to the facility. Utilizing forest and milling residuals along with other woody feedstocks allows for exceptionally low carbon intensity for collection of raw materials. Co- production of power from the gasification and F-T sections of the process allow reduction in carbon intensity do to co-product credits which result in negative carbon intensity for fuel production with some plant configurations and location.

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

### **KEYNOTE ADDRESS: THE NEED FOR SUSTAINABLE LIQUID FUEL AND THE PROMISE OF ADVANCED BIOFUELS**

Don Scott

Liquid fuels are profoundly important to our society. Liquid fuels are the densest, safest, and most economical way to store energy for a myriad of uses. We rely on liquid fuel to harvest and distribute food. We rely on liquid fuels to transport goods and people. We rely on liquid fuels for emergency vehicles and backup electrical power as just a few examples of its importance. Fossil fuels and petroleum, in particular, are now criticized for greenhouse gas (GHG) emissions and dwindling reserves of crude oil. Sustainability is a measured balance of environmental, economic, and social factors. Our growing global population and current standard of living cannot be sustained without liquid fuel. The challenge faced by the liquid fuels industry is to manage environmental impacts and leverage existing reserves in ways that make the liquid fuels industry sustainable. Major oil consuming nations have already enacted policies that relegate a small percentage of their liquid fuels market to renewable fuels. These policies require renewable fuels to meet specific GHG reductions and often impose additional sustainability requirements. The renewable fuels with the greatest sustainability benefits are being dubbed Advanced Biofuels. This report will detail how the sustainability of Advanced Biofuels is measured and how they can improve the sustainability of the larger liquid fuels industry.

### **PROGRESS MADE TOWARD THE USE OF JET FUEL IN DIESEL-POWERED AIRCRAFT**

*Roger G. Gaughan*

The practice of fitting diesel (compression ignition or CI) engines to general aviation aircraft has continued with aviation authorities around the world certificating aircraft with CI engines to run on jet fuel. Recently it was recognized that a few jet fuel properties were not fully considered during the engine certification process. The aviation industry responded rapidly and has made significant progress in identifying key jet fuel properties that impact CI engine operations in an effort to mitigate any potential fuel property issues. Ignition quality, low temperature and

lubricity constitute the fuel properties currently being evaluated. Progress made toward developing fuels/standards to be used for the certification process will be discussed.

## **BULK DIESEL FUEL FILTRATION – A SENSIBLE INVESTMENT**

*Christian M. Bauer*

Modern surface mine sites and commercial freight railroads are among the world's largest consumers of diesel fuel. For example, a typical mine site can consume over 200 million liters of diesel fuel per year. Delivered diesel fuel is not necessarily clean. Depending on the mode of transportation, handling practices and local climate, incoming bulk fuel can contain as much as 20 mg/L suspended solid contaminants, and, in some locations, also significant quantities of free water. Standard on-board fuel filters, due to the inherent size and space restrictions, are not designed to handle high levels of contamination without significant impact on service life, and most engine manufacturers have specific fuel cleanliness requirements to ensure reliable engine operation. New developments in fuel injector technology, such as high pressure, common rail injectors require even cleaner fuel. Therefore, particulate and water contamination in diesel fuel must be controlled throughout the entire fuel supply chain, from the bulk storage and filling points to the injection systems on-board engines, through the use of particulate filtration and liquid coalescence technologies. In this work, the author introduces a comprehensive approach to contamination control for the entire fuel supply chain, and discusses the benefits of using advanced filtration and separation technologies, with a particular focus on the requirements of modern high pressure, common rail fuel injection systems.

## **IN-LINE MEASUREMENT OF FAME CONCENTRATIONS IN JET FUELS**

*Kam Mohajer*

Increasing government mandates for biofuels, and in particular biodiesel or FAME, have led to FAME contamination issues for producers, shippers, and consumers of jet fuel. Because jet fuel often shares pipelines or tankers with biodiesel, it's at risk of contamination that can lead to serious engine operability issues. While FAME can be detected in the laboratory, there is currently no in-line measurement tool. Laboratory measurement is extremely costly in terms of capital, time, man-hours, demurrage, etc. In-line measurement provides real-time data generated within the supply chain, greatly increasing the efficiency with which operators can identify FAME concentrations and compliance with mandated FAME contamination limits. KAM CONTROLS, INC. has developed an optical, in-line FAME meter that can be inserted into pipelines or incorporated into an analysis loop. This FAME meter provides real-time data compliant with industry and government requirements for accuracy and repeatability. It measures FAME to concentrations of 1 to 150 ppm, regardless of type of jet fuel, aromatics, refining process (Merox or hydrotreated), or type of FAME. The development of the FAME meter provides the military, airline, pipeline, and refining industries with reliable, cost-effective, real-time data that eliminates the delays and laboratory costs associated with current methods. Ongoing, real-time measurement of FAME concentrations enables ALL jet fuel to be accurately tested at key stages in the supply chain, greatly increasing the confidence of producers, pipeline operators, and end-users in the safety of all jet fuel product.

## **JET FUEL DEGRADATION DURING SUPERCRITICAL HIGH HEAT FLUX HEAT TRANSFER**

*Zachary J. West, Hua Jiang, Jamie S. Ervin, and Steven Zabarnick*

Kerosene jet fuels play an important role as an onboard engine coolant in military aircraft. The efficient use of jet fuel as a coolant can be challenged as aircraft and engine components experience much higher heat fluxes due to supersonic and hypersonic flight conditions. Therefore, the use of jet fuel as a coolant under high heat flux heat conditions was examined both experimentally and computationally. The results highlight the intricate relationship between thermodynamic, fluid dynamic, and chemical kinetic behavior of jet fuels during supercritical forced convective heat transfer. Results suggest that extra care should be taken when designing heat exchange components that experience high heat fluxes.

## **JET FUEL DESULPHURISATION: AN INVESTIGATION INTO THE IMPACT OF HYDRO-TREATMENT ON PRODUCT QUALITY**

*Jeremy Tucker, Christopher Lewis, Alisdair Clark*

Defence Standard 91-91 and ASTM D1655 specifications currently limit jet fuel sulphur content to a maximum of 3000 ppm. While market survey data indicates regional averages are significantly below this, typically in the range 240 to 730 ppm, the Aviation Industry are seeking to determine the impact of moving to a lower sulphur product for environmental benefit. Such a transition has broad implications and one of the most important is to determine the systematic shift in fuel quality. Modern turbine engines are designed to give high reliability over many thousands of hours of operation and any significant change to the fuel consumed during this period requires assessment, both in terms of possible issues and benefits. In this paper the effect of progressively desulphurising jet fuel from 2200 ppm to 10 ppm by hydro-treatment has been examined. Trends in product quality are presented with particular focus on lubricity, energy content and thermal stability. Where appropriate, new analytical techniques have been applied to gain further insight into the changes taking place. In conclusion, the paper draws together the technical information to highlight the changes which may be expected in moving to a lower sulphur jet and how these might offer benefits and challenges for Industry appraisal.

## **INVESTIGATION OF ELASTOMER COMPATIBILITY WITH ALTERNATIVE FUELS BY MASS CHANGE STUDY, STRESS-RELAXATION TEST AND FTIR SPECTROSCOPY**

*Yue Liu, Christopher W. Wilson, Simon G. Blakey and Patrick Theato*

Global efforts to reduce CO<sub>2</sub> emissions and to tackle the problem of depleting petroleum resources have stimulated the exploitation of alternative fuels in the aviation industry. One crucial aspect amongst others is to investigate the compatibility of alternative fuels with elastomeric materials currently used in gas turbine engines. However, limited knowledge about this has been understood so far for commercial aircrafts under real engine conditions. This study combines Stress-Relaxation test and FTIR spectroscopy techniques to look at the effect of

alternative fuels on O-rings made from different materials; such as nitrile, fluorocarbon and fluorosilicone. Mass change behaviors of these O-rings immersed in various solvents were also monitored to compare with the stress relaxation results. Results indicated that both fluorosilicone and fluorocarbon O-rings showed excellent compatibility with the candidate solvents, whilst nitrile O-rings were very sensitive to the different compositions of the solvents. Mass change behavior of nitrile O-ring also showed similar pattern to those of its stress relaxation. FTIR spectrum analysis showed molecular composition changes are dependent on the reactions between different materials and solvents. For fluorosilicone O-rings, the absorbance reduction from 1150 to 1050 cm<sup>-1</sup> was caused by the cleavage of (Si-O-Si) while the formation of new O-H bonds enhanced the intensity from 3000 to 2800 cm<sup>-1</sup>. For fluorocarbon O-rings, obvious increase in absorption could be found in the region from 1400 to 650 cm<sup>-1</sup>, while from 3000 to 2800 cm<sup>-1</sup>, the absorption decreased. Multiple linear regression analysis indicated a highly correlated relationship between the chemical structure changes and the force relaxation.

### **CONTAMINANTS FOUND ON DIESEL FUEL STORAGE TANK FILTERS**

*Joseph Block, Paul Klick, James Doyle, Philip Johnson, and Andrew J. Dallas, Yehya Elsayed, PhD*

As simple as the theoretical storage of diesel fuel should be, it is actually fraught with significant issues. Diesel fuel is believed to be transported and delivered into a storage tank at a given specified cleanliness level, which is thought to be maintained throughout the storage duration. However, it is well documented that rapid fuel filter plugging often occur upon pumping pre-filtered fuels. This study will address several examples of observations made from field samples of diesel fuels taken from plugged storage tank filtration applications. It will focus on the evaluation and characterization of the materials found on plugged diesel fuel filters. A case will be made for new fuel filterability requirements and standards in order to ensure diesel fuels can be suitably cleaned to meet the requirements of modern fuel injector system designs.

## **SESSION 3: AVIATION FUELS TODAY AND TOMORROW**

### **OVERVIEW OF U.S. NAVY'S RENEWABLE TURBINE FUELS EVALUATION**

*Andrew McDaniel, Richard Kamin Sherry Williams<sup>1</sup>, John Buffin, Dr. Geoffrey Eldridge, Jennings Bryant, and Glen Fetsch*

The United States Navy has been evaluating non-petroleum sourced alternative fuels for use as a military aviation turbine fuel replacement. The Navy requires that any alternative sourced fuels be drop-in replacements that require no modification to existing propulsion systems. Included in this testing are various hydrotreated renewable jet fuels and 50/50 blends of renewable/petroleum jet fuel. Laboratory testing of chemical and physical properties performed on each fuel showed similar or improved properties when compared to 100% petroleum sourced fuels. Performance testing, which includes fuel handling, materials, engine component, and full-scale engine testing, has been conducted for multiple aviation propulsion systems. Flight demonstration using a 50% alternative sourced fuel was conducted on various naval aircraft platforms. This paper will

present the current status and results of the United States Navy's program to evaluate alternative sourced jet fuels.

### **AN EVALUATION OF SYNTHETIC JET FUEL CONTAINING AROMATICS**

*Clifford A. Moses, Petrus N.J. Roets, Mariam Ajam, Carl L. Viljoen, and George R. Wilson, III*

Due to the implementation of more stringent environmental regulations in South Africa, Sasol is required to reduce the benzene content of all grades of petrol. An economically viable option is to remove the benzene and then use it as a co-feed to the olefin oligomerization plant; this plant makes the iso-paraffinic kerosene (IPK) used for the last 11 years to blend semi-synthetic jet fuel (SSJF). Changing the feed composition to this plant has the result that the IPK will now contain alkylated mono-aromatics as part of the composition. The fit-for-purpose tests of ASTM D4054 have been conducted, and this new synthesized kerosene has been shown to have all the same properties and characteristics as conventional jet fuel. Hydrocarbon analysis by 2-dimensional gas chromatography (2-D GC or GCxGC) has demonstrated that all of the aromatics are single-ring aromatics distributed from C9 to C14. Furthermore, these aromatics are all found in the petroleum-derived Jet A-1 that Sasol produces. Therefore, there will be no new chemistry involved in the use of this synthesized paraffinic kerosene with aromatics (SKA) in blending SSJF.

### **NEW ROUTE FOR INCREASING THE AVIATION ALTERNATIVE FUELS PRODUCTION AND OPTIMIZING THE BIOMASS USAGE: FOCUS ON HRJ**

*Laurie Starck, Ludivine Pidol, Nicolas Jeuland, Thierry Chapus, Joanna Bauldrey*

Both Fischer-Tropsch (FT) and Hydroprocessed Renewable Jet (HRJ) synthetic paraffinic kerosene (SPK) fuels are considered as the leading alternative replacements for conventional jet fuel. To satisfy the requirements of Civil Aviation Authorities (CAAs), their drop-in incorporations have been subjected to a rigorous certification process. In order to reach the ambitious incorporation targets, new routes for biofuels incorporation should emerge, involving optimizing the production processes and the blending strategies. This paper focuses on a new incorporation strategy for HRJs, allowing an optimization of the process yield. One of the major steps limiting the process yield for HRJ remains the isomerisation that allows production of a biofuel with very good cold flow properties. But this step introduces a substantial decrease of the global yield (fuel component per kg of starting material) due to the production of light compounds, unsuitable for conventional jet fuel. So, this work proposes lowering the freezing point requirement of HRJ (by decreasing the severity of the isomerisation step), to maximize the HRJ jet fuel yield, while maintaining the attainment of final jet fuel specification requirements after blending. This strategy could lead to a significant additional jet fuel yield with respect to the oil. This allows reduction of the necessary land surface area to culture the plant, for a given amount of bio-jet fuel produced.



## **SELECTED ENGINEERING PROPERTIES OF AVIATION TURBINE FUELS**

*Scott A. Hutzler and George R. Wilson*

Working closely with fuel producers, air framers, engine manufacturers, and the U.S Air Force, Southwest Research Institute (SwRI) has had the opportunity to investigate a variety of emerging synthetic jet fuels. The two most widely recognized types of synthetic jet fuel components are paraffinic kerosenes from the Fischer-Tropsch (FT SPK) process and from Hydroprocessed Esters and Fatty Acids (HEFA). These fuels have undergone a rigorous examination to gain approval for use as drop-in replacements for current aviation turbine fuels. In the early stages of the approval process, some obvious differences in chemical composition, such as the iso/normal paraffin ratio and low aromatic content, raised concerns about the performance of these fuels relative to current experience. Through ASTM, the approval process for candidate aviation fuels was revised to include fit-for-purpose testing beyond the scope of standard jet fuel specifications. In this paper, we will explore some of the unique chemical and physical characteristics of refined jet fuel, synthetic jet components, selected suggested alternative chemistries and blends thereof. This information will be used to evaluate their effect on bulk properties relative to petroleum-based fuels. In particular, less familiar tests such as dielectric constant, thermal conductivity, and bulk modulus will be examined. The results will show that the compositional differences have predictable effects on fuel properties which in most cases have little or no impact on fuel performance.

## **EVALUATION OF THE ALTERNATIVE FUEL THERMAL STABILITY WITHIN THE EUROPEAN SWAFEA PROGRAM**

*Mickaël Sicard, Laurie Starck, Simon Blakey, Jacques Ancelle, Nicolas Jeuland, Aurélie Pipere, Bruno Raepsaet, Frédéric Ser, Thomas Spalton, and Christopher W. Wilson*

The thermal stresses imposed on aviation fuels by aero-engines can lead to the formation of deposits within engine fuel systems which, in turn, can reduce their performance and necessitates extra maintenance to rectify. As modern and developing aero-engines subject fuels to ever increasing levels of thermal stress, the significance of fuel-thermal-stability is becoming more important. Therefore, it is increasingly beneficial to use fuels which minimize the formation of these undesirable deposits at high temperatures. Different fuels demonstrate varying levels of thermal stability, largely due to their chemical composition. The presence of dissolved oxygen plays a major role in the degradation of the fuel and in the formation of insoluble products. The standard test method used to estimate the thermal oxidation stability of aviation turbine fuels is the JFTOT Procedure. All the fuels tested in the European Swafea project pass the test. Thus, it was not possible to observe any thermal stability difference between the selected fuels. In order to get more information on their oxidation behaviors, three specific tests are used. The sensitivity of the fuels to oxidation stability is determined. The most sensitive fuel is the blend 50% Camelina/50% Naphthenic followed by the blend 75% Camelina/25% Jet A-1. This result is confirmed as these fuels contain the highest quantity of oxidized products observed in the liquid phase after 72 hours of degradation. These two blends produce the lowest quantity of deposit. On the other hand, the Jet A-1 and the blend 90% Jet A-1, 10% FAE seem to be the least sensitive to oxygen, conversely it produced the highest quantity of solids. Thus, the thermal stability is directly linked to the fuel composition. The neat fuels (HVO Camelina and Naphthenic-

aromatic) do not contain natural oxidant. So when blended, they show the lowest oxidative stability but they demonstrate the highest thermal stability as they do not produce deposit.

## **ANALYSIS OF PROPERTIES OF JET FUEL PRODUCED BY COCONUT OIL**

*Zhiping Tao, Dongmei Gong, Hongliang Qu*

We developed a process to coconut oil as raw material to produce bio-jet fuel. This process first used hydrogenation removal of oxide in coconut oil, and further hydroisomerization and hydrocracking to produce distillate jet fuel. In the laboratory, their physical and chemical properties is tested according to the requirements of ASTM D7566, while using GC-MS analysis of the carbon number distribution. The performance numbers in full compliance with GB65373 jet fuel requirements that was tested at a blend ratio of up to 50 percent with traditional jet fuel (No. 3 or Jet A-1).

## **IMPACT OF FUEL COMPOSITION ON EMISSIONS AND PERFORMANCE OF GTL KEROSENE BLENDS IN A CESSNA CITATION II**

*Tim A. Snijders, Joris A. Melkert, Joanna M. Bauldreay, Paul F. Bogers, Claus R. M. Wahl and Manfred G. Kapernaum*

International jet fuel specifications permit up to 50% volume Fischer-Tropsch synthetic paraffinic kerosines (FT-SPKs), such as Gas-to-Liquids (GTL) Kerosine, in Jet A-1. The 50% limit relates mainly to having 8% aromatics in the fuel, to ensure adequate o-ring swell. Higher SPK-containing fuels could, however, produce desirable fuels: lower density, higher SPK-content fuels may have benefits for Payload range (PLR) performance and their chemistry should improve many engine emissions. GTL-containing fuels have been tested in a Cessna Citation II, with P&W Canada JT15D-4 turbofan engines: earlier laboratory and rig tests on high GTL content fuels led the Dutch aviation authorities to permit operating the aircraft for experimental purposes. Ground tests (with performance, post test inspections and emissions measurements) have been run prior to dual-fuelled flight tests, which will generate side-by-side data to check PLR modelling. Specifically, one engine has been run according to ICAO power settings and probes behind the engine have captured gaseous and particulate emissions. Data will be presented for fuels with 0-50% GTL contents, tested at 6 conditions between and including idle and full thrust. Filters that remove particulates in gaseous emissions lines clearly indicate a progressive improvement with increasing GTL/decreasing total aromatics content. At all engine settings, the particle diameter, emission index in terms of particle number and emission index in terms of particle mass all decrease significantly with GTL content. For gaseous emissions, emissions indices for NO, NO<sub>2</sub>, NO<sub>x</sub> (NO+NO<sub>2</sub>), SO<sub>2</sub> and CO have been tracked for each engine setting. There is a very small reduction of NO<sub>x</sub> at higher power settings and a 5-10% reduction on CO emissions for 50% GTL at most engine conditions. SO<sub>2</sub> reductions are seen clearly for the higher sulphur base fuel blends.

## **SESSION 4: FUEL FILTRATION AND CLEANLINESS**

### **THE EFFECTS OF FAME CONTAMINATION IN F34 ON API/EI 1581 FILTRATION SYSTEMS**

*Gary Bessee and Jerry Tucker*

This program was performed to determine the effects of FAME contaminated F-34 aviation fuel on filtration performance utilizing EI 1581 5th Edition test protocol; using EI 1581 5th Edition M and EI 1581 3rd Edition C category coalescer/separators purchased from various suppliers as required by the MOD. The objective of this program was to determine if the current acceptable FAME concentration (5-ppm) could be raised to 100-ppm without causing filtration issues.

Baseline testing was performed utilizing elements from all of the major aviation filtration manufacturers. EI 1581 5th Edition evaluations were then performed in duplicate with 400-ppm FAME contamination per ASTM D4054 (4X). Gravimetric, aqua-glo, and electric sensor (particle counting and turbidity) data was obtained for all of the evaluations. Three of the four filtration systems passed both the EI 1581 5th Edition baseline and EI 1581 5th Edition 400-ppm FAME contamination evaluations. Although three systems passed, there was some reduction in filtration performance for two of the filtration systems.

### **THE USE OF LIGHT OBSCURATION PARTICLE COUNTING TO STUDY DISPERSED SOLID CONTAMINATION IN AVIATION TURBINE FUEL AT KANDAHAR AIRBASE, AFGHANISTAN**

*Matthew Fielder and Supreme Fuels*

It has been widely recognised throughout the aviation industry that the current specifications Test Methods for determining particulate matter are both inadequate and subjective. ASTM-D-4176 is a purely visual test, hence its subjectivity. ASTM-D-5452 is a more accurate analysis based on a gravimetric determination of suspended solids, but again this lacks suitable specific data to assess particulate contamination throughout an aviation fuel supply and storage chain. Specialist instruments are available that can be used to sample fuel at any point throughout the jet supply line, from the refinery through to the point of aircraft upload. Particle Counting is now included in DEF STAN 91-91 as a report only requirement at the point of manufacture, using Energy Institute Test Method IP564. It should also be noted that in accordance with DEFSTAN 91-91 and CHECK LIST, it is the Specification Authorities intention to replace the determination of particulate contamination at the point of manufacture by D-5452 with particle counting at the earliest opportunity. The development of this method for real time monitoring of dispersed solids in fuels upstream of the Refinery and Supply Terminals is ongoing within the industry, but Supreme Fuels are pioneering the use of this type of equipment in the field and have found that they can provide valuable data in a wide range of applications to determine potential areas of concern on a qualitative and quantitative basis throughout the supply and storage system. This paper is based on Supreme Fuels development of field sampling quality procedures to look at areas of possible contamination throughout its fuel supply and storage facilities in Kandahar, Afghanistan. With systematic Particle Counting analysis throughout the fuel delivery and storage chain, Supreme Fuels have demonstrated the effectiveness of its quality systems in

its operations, thus delivering fuel of a verifiable cleanliness directly to the customer in the most uncompromising of environments.

## **A MAPPING PROTOCOL FOR MEASURING THE WATER SEPARATION PERFORMANCE OF COALESCERS AND/OR ADDITIVES**

*Paul P. Wells, Dennis H. Hoskin*

The current qualification protocol for aviation fuel filter coalescers, EI 1581, specifies a series of dirt and water challenges at rated fuel flow. The filter coalescer is qualified as long as particulate and free water content of the effluent remains below specified levels. The results obtained in EI 1581 testing are not very useful for comparing the relative performance of filter coalescers. Further the resource requirements of EI 1581 are challenging with respect to the amount of fuel and time required for testing. ExxonMobil has developed a novel test protocol that better defines the true filtration performance of the filter coalescers. The protocol involves “mapping” a two dimensional space defined by fuel flow and water injection rate. The curve generated outlines the area above which effluent free water content of 15 ppm (or an alternate specified level) is exceeded. A series of these curves, representing different filter coalescer contaminant loading levels, base fuels, and additive content, can be generated to readily compare water coalescence performance. Compared to EI 1581, this “mapping” protocol requires much less fuel and additive, requires significantly less time, and lends itself to comparative analysis of one system (i.e., any combination of fuel, additive, and filter coalescer) to another. The use of this protocol is illustrated with mapping results from +100 additives.

## **DETERMINATION OF WATER DROPLET SIZE IN DIESEL AND AVIATION FUELS**

*Gary Bessee*

This program determined the water droplet size distributions in diesel and aviation fuels to provide a better understanding of the effects of interfacial tension (IFT) and water separation characteristics of fuels with and without fuel additives. A laser diffraction system was utilized to measure the water droplet distributions. Ultra-low sulfur diesel fuel (ULSD) was utilized using a SAE J1488 water emulsion test stand to determine the water droplet distribution in automotive systems. The test stand uses a 3,500-rpm centrifugal pump to generate the fuel/water emulsion. Clay-treated ULSD was utilized as the baseline fuel. Mono-olein was used as a biodiesel stimulant to lower the IFT to determine if the water droplet distribution changed as a function of IFT. It was shown that the water droplet distribution for the baseline ULSD with an IFT of approximately 32 mN/m had a D50 of approximately 13-micron. Reducing the IFT to 12-14 mN/m reduced the D50 water droplet size to approximately 6-7 microns. This reduction in droplet size distribution resulted in significant reduction of water removal efficiency when evaluated the same automotive filters per SAE J1488. Similar analysis using aviation fuel and typical aviation fuel additives (Static dissipater additive (SDA), corrosion inhibitor (DCI4A, fuel system icing inhibitor (FSII), and thermal stability additive (+100) is on-going with results expected prior to the IASH 2011 meeting.

## **WATER SEPARATION PERFORMANCE OF +100 ADDITIVES**

*Paul P. Wells, Dennis H. Hoskin, Andrew Sutkowski*

Infineum and ExxonMobil have developed a new +100 additive with improved water separation performance compared to the currently approved product. JP-8+100 jet fuel was developed by the U.S. Air Force to provide improved thermal stability/reduced fouling in high performance military aircraft. Typical +100 additives include some level of surface activity to disperse deposit precursors. Unless properly designed and formulated, the surface-active nature of the +100 additive can negatively impact the water separation characteristics of the additized fuel in filter/coalescer systems. The surface activity of the Infineum/ExxonMobil +100 additive was optimized to enable “filter friendly” performance. To document this advantage, ExxonMobil has developed a novel test protocol that better defines the impact of jet fuel additives on filter/coalescer performance. The protocol involves “mapping” a two-dimensional space defined by fuel flow and water injection rate. The curve generated outlines the area above which the effluent free water content of interest is exceeded. The curves generated from the new and existing approved +100 additives are compared demonstrating significant improvement in filter friendly performance for the Infineum/ExxonMobil additive. ExxonMobil/Infineum also applied the mapping protocol to assess the impact of various additive manufacturing/finishing options on the filter friendly performance of the final product.

## **SESSION 5A: ANALYTICAL METHODS**

### **QUANTIFICATION OF PIPELINE DRAG REDUCING ADDITIVE IN JET FUEL TO PPB LEVELS**

David J Abdallah, Dennis H. Hoskin, Barb A. Whittaker, and Paul C. Naegely

Drag Reducing Additive (DRA) contamination in jet fuel is a potential risk to aviation safety. It is often injected into fuels that run alongside jet fuel during pipeline transport. DRA is not allowed in jet fuel and although pipelines have procedures in place to mitigate the risk contamination could still happen. A review of the data indicates that low ppm levels are known to significantly reduce the atomization of fuel sprayed from fuel nozzles and make engine starting more challenging. No safe limit has been determined and there are currently no requirements for monitoring DRA contamination in jet fuels. In an effort to address this risk, an ASTM task force with a mission to develop a quantification method for detecting DRA in jet fuel was formed. Available methods for detecting DRA in jet fuel only extend to low ppm levels. Seeing that low ppm levels can cause problems in aviation turbine engines detection methods are needed that go beyond the current detection limits. A method based on rotoevaporation/GPC total exclusion has been developed that can extend DRA detection in jet fuel down to 50 ppb. The method uses standard refractive index detection and commonly accepted heptane as a mobile phase making it highly deployable to a variety of labs. This paper reviews the current methodologies to quantifying DRA in jet fuel and describes the benefits and trade-offs to employing GPC total exclusion.

## **ADVANCEMENTS IN THE DEVELOPMENT OF FLOW ANALYSIS BY FTIR SPECTROSCOPY IN A RAPID SCREENING TEST METHOD FOR MEASURING TRACES OF FATTY ACID METHYL ESTERS IN AVIATION TURBINE FUELS**

*Paul Spitteler and Ian Mylrea*

As reported at the IASH meeting in Prague in 2009 the Energy Institute conducted a program to publish IP methods to measure FAME contamination levels in aviation fuel. Two chromatography methods (IP590, IP585) and a fully automated rapid screening method IP583 based on flow analysis by FTIR were published in 2010. The flow analysis by FTIR method utilises a sampling technique that retains the FAME component from the sample under test using a sorbent cartridge. The fuel is then analysed by infrared in relation to the untreated fuel. Research has shown that other components present in the fuel could in some cases have an effect on the test result. This paper will discuss the implementation of a PLS-1 chemometrics model, the performance improvements due to this technique, its conformance to E1655 and the results and statistical analysis of a worldwide sample testing programme.

## **EVALUATION OF A RAPID SCREENING METHOD FOR MEASURING FAME IN JET FUELS**

*David J Abdallah, Dennis H. Hoskin, and Paul P Wells*

Measuring Fatty Acid Methyl Ester (FAME) contamination in jet fuel has become increasingly important now that biodiesel and jet fuel share common pipelines and transportation vessels. Mid infrared spectroscopy is a powerful tool for analyzing the presence of compounds with ester functional groups. The infrared stretching frequency of the carbonyl group produces one of the most intense infrared absorptions permitting low ppm detection of FAME contamination in jet fuel. Further improvements are made by removing background absorptions. An effective jet fuel background sample can be prepared by passing the contaminated jet fuel through a sorbent cartridge which strips away the FAME components. Subtracting the spectrum of the background fuel from the contaminated fuel results in a highly resolved spectrum of the FAME components which can be modeled to quantify the FAME concentration. Seta Analytics developed an instrument called FIJI (FAME In Jet Instrument) that automates this process. FIJI applies a proprietary PLS-1 chemometrics model to analyze the infrared difference spectrum. The proprietary model was tested for its ability to handle a wide range of jet fuels and FAME types. Our evaluation revealed that jet fuels produced at different refineries with different crude slates and upgrading processes can lead to bias in the measurement by as much as 10 ppm. The bias is created by the extraction of other polar components present in the uncontaminated jet fuel. An evaluation of the impact of FAME chain length found that the concentration of methyl esters with long fatty acid chains are underestimated while short chains are overestimated (relative to a C18 chain length) and ethyl esters are highly underestimated. Lastly, the impact of a variety of standard jet fuel additives revealed none interfered with the measurements at their highest allowable concentrations.

## **ADVANCEMENTS IN THE MEASUREMENT OF LIQUID PHASE HYDROGEN SULPHIDE (H<sub>2</sub>S) IN MARINE FUELS AND CRUDE OILS**

**Ian Mylrea, Wanda Fabriek and Paul Spitteler**

Hydrogen Sulfide (H<sub>2</sub>S) is a toxic gas which can be present in liquid fuels and crude oils. Safe atmospheric exposure limits are at very low parts per million levels. H<sub>2</sub>S present in liquid fuels is not stable and the gas can be released by agitation, heat or during storage. In the presence of water, H<sub>2</sub>S forms highly corrosive Sulphuric Acid. It is important that cargoes are analysed for H<sub>2</sub>S so that they can be handled safely. In July 2012 the marine fuel specification, ISO 8217:2010 will make it obligatory for marine fuels, meeting ISO 8217:2010, to contain less than 2 mg/kg of H<sub>2</sub>S. UK Energy Institute Test Method IP 570 was issued in 2009. Feedback from users of the new test method has shown some cargoes reporting H<sub>2</sub>S were not treatable by scavenger. Unusual response curves were found. Light Cycle Oil, which is typically high in Sulphur, gave a similar response. Research showed that the detector used in the method was sensitive to chemicals found in LCO's. Research into the measurement of H<sub>2</sub>S in crude oil demonstrated similar cross sensitivity. A joint project with the Canadian Crude Quality Technical Association was formed with the goal of further developing the technique to handle high concentrations of H<sub>2</sub>S and contaminants. A new innovative method has been developed to reliably remove the components in marine fuels and crude oils which cause unusual response curves and give a more precise determination of the amount of H<sub>2</sub>S present in the fuel. This paper will discuss the user feedback and the development of the new techniques developed to reduce cross sensitivity for both marine and crude oils to enable the industry to accurately determine the concentration of H<sub>2</sub>S at low (mg/kg) levels.

## **SESSION 5B: ANALYTICAL METHODS**

### **ROUND ROBIN TEST RESULTS FOR FALEX 400, A NEW JET FUEL THERMAL OXIDATION TESTER, AND HEATER TUBES FOR ASTM D 3241**

*Jim Hepp*

This paper presents a new commercially available jet fuel thermal oxidation test instrument and test specimens, designed to run ASTM D 3241. The paper will detail round robin tests results of the instrument and test specimens that show these products produce equivalent results existing ASTM D3241 test instruments and test specimens. The heater tube tests were run as prescribed in the D 1550 test requirements set out by ASTM subcommittee J. Breakpoint results for the Falex 400 was compared directly to existing D 3241 test equipment in three independent labs running the same 12 fuels in each lab. ASTM D3241 further requires a strict conformance to instrument and heater tube requirements (table 2) for the jet fuel industry for this critical test. The Falex 400 and heater tubes have been shown to match results of existing test instruments and test specimens because Falex has dutifully included the critical equipment specification that controls the heater test section and the test conditions. Designed for years of long operation, the reliable Falex 400 provides traceability, long maintenance intervals and pour-and-go technology, where simply pour your sample into a beaker, push a button and D 3241 is run.

## **RESURRECTION OF THE ELLIPSOMETER AS AN ABSOLUTE WAY TO MEASURE D 3241 DEPOSITS**

*Ervin Schlepp*

IP PM-DD 05 is an IP proposed method for using an instrument called an Ellipsometer to rate heater tubes for IP 323. This paper presents a new, commercially available, Ellipsometer designed to perform the IP PM-DD 05 test method. Discussion the basic principles of Ellipsometry will be provided including how measurement of heater tube film deposits in nanometer thickness are made via this technique. Related Standards are ASTM D 3241 and SAE APR5996. The primary tools for collecting Ellipsometry data all include the following: light source, transmission optics for polarization, sample, analyzer optics, detector, and data acquisition. The transmitter is constructed of optical components that manipulate a light source into a known polarized state. The polarizer light is transmitted onto the surface of the sample heater tube and the reflected light is captured by analyzer optics. The captured reflected light polarization is measured and converted into an electrical signal for analysis and film thickness calculation. Components included are polarized light source, collimator, polarizer, compensator (1/4 wave) focal lenses, sample holder with linear and rotating capability, rotating analyzer with polarizer, photo detector, data acquisition and analyzing software. The design of this new instrument with state of the art components will be discussed, focusing on the critical parameters that have been controlled to enhance the accuracy of the instrument. Finally, tests from this equipment comparing Ellipsometer results to Visual Tube Rating will be presented.

## **PRECISION AND RELIABILITY OF BREAKPOINT TESTING**

*George R. Wilson, III*

While the most common use of ASTM D3241 is for specification conformance, the reliability of that effort is based on the understanding of the nature of relative thermal oxidative stability. The evaluation of relative thermal oxidative stability is the result of a series of D3241 determinations from which the result is called the breakpoint. This paper will first review the history of the breakpoint method and its fundamental relationship to turbine engine performance. Following that the paper describes the current breakpoint procedure and illustrates the way in which it works. Next there will be a more in depth review of how breakpoint relates to hardware performance and how that knowledge is used to manage the methodology. Finally there will be a review of the results from several programs that evaluated the precision of the test method using breakpoint evaluation. With the referenced information the author will offer a series of recommendations on how the industry should proceed with breakpoint methodology in the future.



## **ANALYSIS OF THE STRUCTURE OF DEPOSITED MATERIALS AT INNER SURFACE OF JET FUEL INJECTOR FEED ARM WITH OPTICAL AND SCANNING ELECTRON MICROSCOPY**

*Ehsan Alborzi, Simon G. Blakey, Hassan Ghadbeigi, Christophe Pinna1, Mohamed Pourkashanian and Christopher W. Wilson*

An experimental technique was used to reveal the true structure of deposit generated on the inner surface of a jet engine feed arm injector under rigorous condition close to the real jet fuel system. This is represented by a stainless steel tube through which jet fuel passes and is thermally stressed by the application of Aviation Fuel Thermal Stability Test Unit. Subsequently the tube deposit containing was prepared for the surface analysis with Optical Light Microscopy and Scanning Electron Microscopy. In addition, energy dispersed X-ray spectroscopy was used to determine the elemental analysis of the deposit layer.

## **ANALYSIS OF LARGE SCALE THERMAL STABILITY TESTING**

*Simon G. Blakey, Thomas Spalton and Christopher W. Wilson*

The results of thermal stability testing on the Aviation Fuel Thermal Stability Test Unit (AFTSTU) are compared for a range of fuels. Common features in the resultant data have allowed the fitting of data for the temperature rise in a representative burner feed arm tube over the course of the test at various different heat loadings to an empirical relationship. This relationship is of a similar form to that seen in transient heat transfer calculations. Testing of the same fuels has also undertaken using the High Reynolds Number Thermal Stability (HiReTS) rig, both in the EI 482 form and in an adapted mode to represent more closely the AFTSTU test conditions, albeit at a smaller scale. A similar empirical relationship is observed and permits some discussion around the scaling of representative burner feed arm deposition. However, unlike the AFTSTU the HiReTS test provides no other information on the engine fuel system's sensitivity to fuel thermal stability. The adapted HiReTS test is not considered suitable to replace AFTSTU testing; however initial screening work on a smaller scale is attractive in the assessment of the suitability of alternative fuels. The use of an adapted test allows smaller scale thermal stability tests to be carried out on novel and alternative fuels without the need for large volumes of fuel and permits a prediction of their large-scale performance.

## **SESSION 6: PROPERTIES, CHEMISTRY AND VIABILITY OF FUELS**

### **DEVELOPING FUNDAMENTAL RELATIONSHIPS BETWEEN FUEL COMPOSITION AND PERFORMANCE**

*Jeffrey A. Cramer, Nathan Begue, and Robert Morris*

The U.S. Naval Research Laboratory is developing algorithmic modeling capabilities to determine the link between chemical constituency and resultant fuel properties and performance. It is understood that such links exist, but the compositional complexity of hydrocarbon fuels has limited this approach to model fuels and simple surrogate fuels. The goal of this study is to develop a link between the entire composition of a fuel and how it performs in any given

application. This approach will address the limitations of current property specification-based fuel assessment methodologies and provide a framework for determining fit-for-purpose of a fuel in any engine or system, regardless of fuel type or source. This new and broader approach, based on overall fuel constituency, would provide the means to perform more relevant and source-independent fuel quality assessment; to identify suspect fuel supplies more reliably; and to design and implement novel synthetic fuels, biofuels and fuel blends for current and future propulsion and power systems. To achieve the comprehensiveness necessary for the present work, a chemical profiler utilizing gas chromatography–mass spectrometry (GCMS) and/or GC x GC time-of-flight mass spectrometry (GCxGC-TOFMS) were used to develop comprehensive compositional descriptions of a large set of worldwide jet and diesel fuels. Mathematical and chemometric models were then developed to correlate the fuel composition information with fuel properties. The relationships thus derived between individual compounds and fuel properties will be explored in the course of the presentation.

### **HYDROCARBON GROUP-TYPE ANALYSIS OF CURRENT AND FUTURE AVIATION FUELS: COMPARING ASTM D2425 TO GCxGC**

*Richard C. Striebich, Linda M. Shafer, Zachary J. West, Ryan K. Adams, Steven Zabarnick*

Group-type analysis of hydrocarbons in jet fuel is becoming more important as alternative fuels (biojets and fuels from other non-petroleum sources) are developed. While specific chemical composition information may be too involved to relate to fuel properties and performance in a meaningful way, group-type compositional information may be sufficient to predict properties. Specifications are being developed for alternative fuels which limit the quantity of some hydrocarbon classes (e.g., cycloparaffins) in a fuel to establish some uniformity between fuels from different sources. Consequently, methods to quantify classes within fuels are being re-evaluated or developed to better measure the classes in new fuels and sources. An established group-type method, ASTM D2425, is a tedious technique consisting of 2 HPLC separations, 2 MS or GC-MS analyses as well as saturate and aromatic fraction collection. GCxGC is capable of performing a preferable, automated separation of group-types from fuel, applying both mass spectral confirmation and flame ionization detection quantitation for each fuel component. Post-run analysis of complex GCxGC data can be conducted quickly (several minutes) using templates which provide locations for each compound class. Initial results for this contribution show promising similarity between the methods for a series of petroleum-derived fuels. Examples of biojet and bio-derived fuels are also provided and compared to quantitative results obtained by the conventional techniques. The accuracy of GCxGC for cycloalkane determinations in alternative fuels will be discussed.

### **DEVELOPMENT OF A COMPOSITIONAL DEFINITION OF JET AND DIESEL FUELS USING A NOVEL AUTOMATED COMPOUND CLASSIFICATION SCHEME**

*Robert E. Morris, Nathan J. Begue, and Kristina M. Myers*

With the introduction of alternative fuels into fleet inventories has risen the question of what constitutes an acceptable fuel as a drop in replacement for current petroleum based fuels. Current specification based testing may no longer be appropriate and a more compositional based

analysis is desirable. While many studies of specific compound classes on a limited number of fuel samples have been published, a broadly scoped analysis has been lacking. Presented here is an expansive analysis of a library of nearly 1100 worldwide jet and diesel fuels, including petroleum-derived fuels in addition to synthetic and hydrorefined alternative fuels. This survey was possible through the use of a novel automated chemical component classification scheme which is enabled by a set of selection rules that operate on either the molecular formula or IUPAC name from a previously generated “hit list.” Compositional profiles based on chemical compound class, average carbon number, carbon number distributions and degrees of unsaturation have been established. The compositional profile database constitutes a rich source of information that includes lists of compounds that populate each compound class, rates of occurrence of each observed compound by fuel type, and relative concentrations. In addition, the profiler has proven to be a useful tool for rapid interpretation of other GC-MS fuel analyses. A brief overview of the compositional profiler will be given, followed by some examples of its use in interpreting GC-MS data, as well as the compositional information and trends derived through statistical analysis of the compositional profile database.

## **USE OF SURROGATE BLENDS TO EXPLORE COMBUSTION-COMPOSITION LINKS FOR SYNTHETIC PARAFFINIC KEROSINES**

*Joanna M Bauldreay, Paul F Bogers and Ali Al-Sharshani*

Fischer-Tropsch synthetic paraffinic kerosines (FT-SPKs), such as Gas-to-Liquids (GTL) Kerosine, are now accepted as suitable blend components for Jet fuel production, via ASTM D7566. This sets limitations on distillation profiles for the final fuel and neat SPK, and the cycloparaffin content of the neat SPK. The former requirements (T90-T10 and T50-T10 temperature differences for final fuel, and T90-T10 for SPK) ensure that the final fuel will light properly under all conditions. The cycloparaffin limit of 15% mass reflects that no SPK with more cycloparaffin has yet been tested, although crude derived jet fuels usually contain considerably more. SPKs, from FT and other production routes, can be envisaged that would fall outside these limits yet produce perfectly acceptable, even desirable fuels. They are not generally available yet but one can define their compositions in terms of key components (normal paraffins, iso-paraffins and cycloparaffins) and carbon number distributions, derived from 2 dimensional gas chromatography. One can create surrogate blends for combustion-related testing with existing FT kerosines, commercial solvents and laboratory grade single chemicals. Two Technology Readiness Level 3 experimental campaigns have used 5 real and surrogate SPKs in altitude relight and emissions engine tests, with commercial jet fuel also tested to provide a baseline. SPK compositions permitted the impact of the main variables to be determined from the small fuel set. As well as assessing engine/combustor performances, combustion processes were captured with high speed flame imaging and emissions products were speciated and quantified. Details of the SPKs and summarised engine performance results will be presented, with provisional recommendations for relaxing SPK specifications.

## **LOW TEMPERATURE REGIME OXIDATION OF HYDROCARBON FUEL MODELS: AROMATIC OXIDATION, RING CLOSURES AND ALCOHOL FORMATION**

*David J. Evans, Paul M. Rawson and Renée L. Webster*

Hydrotreated fuels have a greater propensity towards oxidation due to the processes lowering the natural anti-oxidant levels. With fuel systems providing a greater role in the thermal management of aircraft systems, the fuel is subject to more elevated temperatures than previously experienced, making it more susceptible to oxidation. The increased heat stress is even greater with the employment of high pressure common rail (HPCR) diesel engines for marine applications due to their increased efficiency and reduced fuel consumption. These engines rely on using a high rate of fuel flow to be used for hydraulic actuation of the injectors and for heat exchange with the large percentage being returned as unburnt fuel. This bypassed fuel can be exposed to temperatures well exceeding 100 °C. Whilst the temperatures experienced in HPCR systems fall into the low temperature regime for fuel oxidation, exposure to these elevated temperatures and pressures accelerates the formation of secondary oxidation products such as alcohols, aldehydes and ketones. The formation of these complexes in the stressed fuel can lead to degradation of important fuel properties such as water separability and filter blocking tendency. We have carried out several thermal stressing experiments that involved exposing a modified surrogate fuel in a cyclic thermal rig at 140 °C and 2700 psi with a residence time of 55 seconds. In order to characterise the oxidation products, some key degradation products were monitored throughout the stressing. With only two aromatic compounds present in the model fuel, viz. toluene and o-xylene, we have quantified the formation of five aromatic derived decomposition products @ 353 ppm after a total residence time of 36 minutes. Several ring closure compounds have also been identified such as iso-benzofuranone and alkylfuranones albeit at low concentrations. The degradation of tetradecane after 36 minutes of thermal stressing was monitored through the formation of tetradecanone and tetradecanol with concentration of 160 ppm and 180 ppm.

## **SPECIATED NAPHTHALENE ANALYSIS IN LIQUID TRANSPORTATION FUELS**

*Linda M. Shafer and Tim Edwards*

Naphthalene (C<sub>10</sub>H<sub>8</sub>) and its substituted derivatives are currently undergoing assessment for their potential toxicological impacts which may result in these compounds becoming regulated. A major source of potential naphthalene exposure in the Department of Defense and throughout the United States are the large volumes of liquid transportation fuels consumed annually (~200 billion gallons domestically), which include gasoline, diesel, and jet fuel. Total naphthalenes data for jet fuels has been reported during a recent study [1], but there is little available data on the concentration levels of individual naphthalene compounds. This paper presents quantitative concentration levels for naphthalene species (namely naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene) and the total naphthalene content in transportation fuels. Speciated naphthalenes were quantified using Gas Chromatography-Mass Spectrometry (GC-MS) with Selected Ion Monitoring (SIM), while High Pressure Liquid Chromatography (HPLC) was used for analysis of the total naphthalenes content. The analysis was performed on a total of 166 discrete fuel samples procured from various locations throughout the world. The three speciated naphthalenes were present in all of the fuels tested, but at much lower concentrations than the

total naphthalenes concentration. Attempts were made to correlate the total and speciated naphthalenes data for the different fuel types. Additionally, the total naphthalenes data for jet fuels analyzed herein were compared to the recent literature study.

## **THE IMPACT OF CETANE IMPROVER ADDITIVE ON THE LUBRICITY OF DIESEL FUEL**

*Ken Mitchell*

Ultra-Low Sulphur Diesel (ULSD), defined as less than 15ppm by mass Sulphur, was introduced in Canada during 2006. To assure that the ULSD as delivered to customers was indeed less than 15 ppm Sulphur some oversight testing was undertaken. In addition to testing for sulphur a number of other parameters were tested. As ULSD requires lubricity additive do be “fit for purpose” samples were tested for lubricity using the High Frequency Reciprocating Rig (HFRR) test, as per the ASTM D6079 test method. Whilst all the results for sulphur content and other measured parameters were as expected some of the HFRR results had significantly higher wear scar diameters than expected which is taken to indicate poor lubricity. Further investigation revealed that all the samples with higher than expected results were from one particular fleet supplied from one Terminal. At this Terminal the lubricity additive is injected at the loading rack as the truck is loaded. It was confirmed that the lubricity additive injection system at this Terminal was operating correctly and metering at the correct rate. The unique aspect was determined to be that the ULSD as supplied to this particular fleet contained 1000 ppm by volume of Cetane Improver Additive (CIA), or 2-Ethyl Hexyl Nitrate. The CIA was injected at the loading rack at the customer’s request. Some further HFRR tests of ULSD samples with varying lubricity additives, levels and varying levels of CIA were then undertaken. The results of these tests confirmed that adding higher levels of CIA to ULSD causes an increase in the HFRR greater than the repeatability of the test (as defined in ASTM D6079). A sample’s HFRR wear scar diameter could be returned back to its original, acceptable, level by increasing the lubricity additive treat rate. This impact of high levels of CIA on lubricity (as measured by the HFRR) was not expected. As we have operated a diesel fuel injection equipment rig test for a number of years (as described in SAE Papers 2001-01-1928, 981363 and 961944) we decided to determine if the negative impact of higher levels of CIA on lubricity, as seen in the HFRR test, was actually seen in real diesel fuel injection equipment. A series of 576 hour diesel fuel injection pump rig tests were run with ULSD samples containing high levels of CIA and varying levels of lubricity additive. The pump rig test results show that this negative impact of CIA on lubricity is solely an artifact of the HFRR lab test and were not seen in the diesel fuel injection equipment tests.

## **CATALYTIC DECOMPOSITION OF HYDROPEROXIDES: IMPLICATIONS FOR JET FUEL STABILITY**

*Zachary J. West, Ryan K. Adams, and Steven Zabarnick*

The autoxidation of jet fuel takes place via a complex free radical reaction mechanism that involves the decomposition of hydroperoxides. The liquid phase, unimolecular decomposition of hydroperoxide has been isolated for experimental study. Three hydroperoxides relevant to jet fuel autoxidation including: cumene hydroperoxide (CHP), dodecane hydroperoxide (DHP), and

ethylbenzene hydroperoxide (EBHP) were thermally decomposed separately and found to closely fit first order behavior with respect to hydroperoxide concentration. The activation energy for liquid phase thermolysis of these hydroperoxides was found to be significantly less than typical gas phase values. Parameters affecting the rate of hydroperoxide decomposition, such as dissolved metal content, organic acids, and metal deactivator additive (MDA) were explored. Metal type was shown to be a significant factor affecting hydroperoxide decomposition rate, while naphthenic acids (NA) were shown to have little effect on the rate. However, when dissolved metal and NA were added together a strong synergistic effect on hydroperoxide decomposition rate was noted. The increases in decomposition rate due to dissolved metal and/or acid were effectively inhibited by treatment with MDA.

## **BEHAVIOUR OF WATER IN AVIATION FUELS AT LOW TEMPERATURES**

*Mark D. Carpenter, Janice I. Hetherington, Liyun Lao, Colin Ramshaw, Hoi Yeung, Joseph K.-W. Lam, Simon Masters, and Sarah Barley*

The presence of water in aviation fuel has been a topic of concern for the aviation industry for many decades since any contaminating water may freeze during long flights at high altitudes creating safety problems. The aim of the present work was to improve the fundamental understanding of the behaviour of water in aviation fuel at the low temperatures experienced during flight. Water droplet and ice formation were studied at temperatures down to  $-60^{\circ}\text{C}$  in a range of jet fuels representative of a Merox fuel, a hydroprocessed fuel and ‘as-received’ fuels from a number of sources world-wide. Parallel studies were carried out in model hydrocarbons representing the aromatic, cyclic and alkane components of jet fuel. The dependence of water droplet and ice particle size was investigated as a function of parameters such as initial water concentration, rate of cooling, fuel composition and hydrocarbon type, and the presence of additives and impurities. Initial studies using low temperature microscopy and particle size analysis indicated that, as the fuel cools, water is released in very fine droplets of size  $5\mu\text{m}$  and below. On cooling the fuel to  $-44^{\circ}\text{C}$  the droplets remained and there was no indication of ice crystal structures being formed. Differential Scanning Calorimetry indicated that the water droplets were supercooling to temperatures as low as  $-40^{\circ}\text{C}$ . The factors affecting droplet formation are discussed.

## **SESSION 7: MIDDLE DISTILLATE FUELS AND HEAVY OILS**

### **CONTROLLING THE STEROL GLUCOSIDES AND SATURATED MONOGLYCERIDES IMPURITIES IN BIODIESEL**

*Marc-André Poirier and Charles Lund*

Cold weather operability and low temperature storage stability are the biggest concerns in much of North America when considering B2+ biodiesel fuels. Although the B100 biodiesel or fatty acid methyl ester (FAME) must meet the ASTM D6751 Standard or the pending CGSB 3.524 Standard “Biodiesel (B100) for Blending in Middle Distillate Fuels”, numerous fuel filter plugging issues have been reported due to impurities precipitating above the cloud point of the fuel. Among the various impurities found in biodiesel the sterol glucosides (SG) and the

saturated monoglycerides (SMG) have been identified as the problematic impurities causing the field problems. The level of sterol glucosides in B100 biodiesel is currently being controlled by the cold soak filtration time (CSFT) test method ASTM D7501. The level of saturated monoglycerides in B100 can be assessed by the Imperial Oil cold soak filter blocking tendency (CSFBT) test method included in the pending CGSB 3.524 Standard. However, there are currently no standard methods to quantify the saturated monoglycerides in biodiesel. To gain a better understanding of the effect of the sterol glucosides, saturated monoglycerides and other impurities precipitating above the cloud point of biodiesel fuel, the distillation characteristics of distilled and un-distilled FAME were examined and compared to CSFBT. The ASTM D1160 distillation temperature limit of 360°C maximum at 90% recovery specified in ASTM D6751 does not protect against the impurities precipitating above the cloud point. The gas chromatography test method ASTM D7398 (SIMDIS) was also examined. The results suggest that ASTM D7398 should be included in ASTM D6751 to control the sterol glucosides and saturated monoglycerides in the FAME.

## **H<sub>2</sub>S IN AND ABOVE FUEL OILS - ANALYSIS AND CONTROL**

*Ivo J. Dijs, Willie Schermer, Remon te Velthuis, Arjen Nieuwhof, Koen Steernberg*

The presence of H<sub>2</sub>S in fuel oils poses a safety risk and consequently, a product quality risk. In fact, this risk is associated to possible exposure of personnel to unsafe H<sub>2</sub>S concentrations in the vapor phase, which may develop due to H<sub>2</sub>S release from the fuel. For analysis and control of this risk it is useful to have information on the H<sub>2</sub>S level that can ultimately develop in the headspace and at the tank hatch opening. Unfortunately, for heavy oils relevant literature information is scarce. Therefore a program was setup to model and measure H<sub>2</sub>S vapor-liquid distributions ratios for various hydrocarbons (e.g. 1-methylnaphthalene, n-hexadecane, gas oils, GTL, residual fuel oil). It was found that ratios for real fuels were lower than values predicted for binary mixtures of n- paraffins and H<sub>2</sub>S. This was attributed to the presence of air and naturally occurring fuel constituents, which can suppress H<sub>2</sub>S. For the absorption of small quantities of H<sub>2</sub>S, fuel composition was also less relevant for heavy fuels than for light fuels. With regard to safety it was concluded that the ISO 8217-2010 limit of max. 2.00 mg/kg H<sub>2</sub>S in fuel oil makes sense, because at this level by rough approximation a headspace concentration of 100 ppmv can develop, and 100 ppmv is also considered by NIOSH as the lowest H<sub>2</sub>S concentration immediately dangerous for life. In addition, H<sub>2</sub>S levels above tank openings will normally be lower due to dispersion. Nevertheless, the ISO 8217-2010 H<sub>2</sub>S limit does not provide a guarantee that the product is handled safely. Therefore safe working and robust monitoring procedures remain important.

## **ABATEMENT OF HYDROGEN SULFIDE FROM ASPHALT STORAGE TANKS**

*Jennifer Draper and Joseph Stark*

The presence of hydrogen sulfide (H<sub>2</sub>S) has long been a safety and environmental concern to all facets of the petroleum industry. Because asphalt contains high levels of H<sub>2</sub>S, it poses a significant risk to individuals involved in its production, storage and distribution. While refined fuels such as gasoline and diesel are typically stripped of H<sub>2</sub>S by distillation or sweetening

processes in the refinery, bottom of the barrel products used for asphalt production do not receive additional processing to remove hydrogen sulfide. Moreover, the high storage temperatures (300 – 400 °F) typical for asphalt generate additional H<sub>2</sub>S from cracking of sulfur compounds inherent in the oil. Hydrogen sulfide concentrations can easily exceed 20,000 ppm (2 %) in the vapor space of asphalt storage tanks and pose a significant health and safety risk to exposed personnel. Local regulations may also limit asphalt production by capping H<sub>2</sub>S emissions from asphalt storage tanks due to air quality or odor concerns. Finally, storage equipment is also put at risk as hydrogen sulfide acts as an aggressive corrodant toward typical metallurgy. The reduction of hydrogen sulfide in asphalt is therefore an important consideration; however, the viscous nature of asphalt, its high storage temperatures and its propensity to continue to produce hydrogen sulfide are obstacles to the efficient reduction of hydrogen sulfide from asphalt storage facilities using conventional scavengers. Difficulties in measuring hydrogen sulfide content in asphalt safely and reproducibly compound the issue. This presentation discusses the use of novel additives for the abatement of hydrogen sulfide in asphalt. These additives demonstrate a high capacity for hydrogen sulfide uptake, are capable of a rapid reaction with H<sub>2</sub>S and are stable at high temperatures. Data from bench scale studies, independent laboratory evaluations, field trials and commercial applications will be presented.

## **SESSION 8: PERFORMANCE ENHANCEMENT: ADDITIVES AND PROCESSING**

### **STUDIES OF LOW-TEMPERATURE OPERABILITY ADDITIVES FOR BIODIESEL BLENDS OF 20% AND LOWER**

*Steven R. Westbrook, Kavitha Moorthy, and Lindsey Hicks*

Thirteen commercially available cold temperature additives were evaluated to determine their effectiveness in improving cold temperature properties of 5% and 20% biodiesel blends. Biodiesels selected for this study were made from different feedstocks; composed of different concentrations of saturated fatty acids; namely yellow grease, palm, rapeseed and soy. The blends were made in No.2 and No.1/No.2 ultra low sulfur diesel fuels. The properties used to screen the additives included cloud, pour, and cold filter plugging points.

### **EVALUATION OF COLD FLOW IMPROVERS IN A MULTI-FUNCTIONAL ADDITIVE SYSTEM DESIGNED FOR USE IN NORTH AMERICAN DIESEL FUEL**

*J. Andrew Waynick*

Ten diesel fuel cold flow additives were evaluated for their ability to provide cold flow improvement when first incorporated as a component in a multi-functional additive system that also includes a detergent/dispersant, corrosion inhibitor, cetane improver, demulsifier, and lubricity improver. Two of the ten cold flow additives were determined to be incompatible with the other components of the multi-functional additive system and were eliminated from further consideration. The remaining eight cold flow additives were evaluated by using them to make the corresponding eight multi-functional additive systems and adding each of them to ten diesel fuels at 1333 ppm (1 part additive per 750 parts fuel). The ten fuels were consisted of eight ultra-



low sulfur and two low sulfur fuels. They were down-elected from a larger set of 24 diesel fuels so as to include a wide range of cold flow improver response. These ten fuels both with and without each of the eight multi-functional additives were evaluated by cloud point (CP), pour point (PP), and cold filter plugging point (CFPP). As expected, CP was essentially invariant to the presence of cold flow improver. Reduction in PP and CFPP varied widely across the ten fuels and the eight additives. Pour point reduction was as low as 2 C and as great as 36°C. CFPP reduction was as great as 18 C, but several fuels actually exhibited an increase in CFPP with several additives. One fuel gave an increase in CFPP with all eight additives. This behavior was due to the fuel's low wax level and the apparent presence of another cold flow improver that was highly antagonistic to the added cold flow improvers. A simple but new method for evaluating cold flow improver additive performance efficiency was used, and the results of this new method was compared to the more standard methods of simple PP and CFPP reduction. The treatment of the data spanning the eight additives and ten fuels allows lessons to be learned as they apply to the interpretation of such data and its application to realistic performance expectations.

## **THE USE OF MBO FOR THE PREVENTION OF MICROBIAL INFLUENCED CORROSION IN STEEL PIPELINES AND TANKS**

*Wolfgang Siegert*

Small amounts of water in a fuel product can cause serious internal corrosion of steel pipelines and tanks used for fuel transportation and distribution. 3,3'-Methylenebis[5-methyloxazolidine] (MBO) shows good corrosion protection according to ISO 7120 (Petroleum products and lubricants; Petroleum oils and other fluids; Determination of rust-preventing characteristics in the presence of water). Additionally the kinetics of corrosion processes of metals can be influenced by growth of microbes in the water phase. Products of their metabolic activities including enzymes, exopolymers, organic and inorganic acids, as well as hydrogen sulphide can affect cathodic and/or anodic reactions, thus altering electrochemistry at the biofilm/metal interface. The dosage of MBO neutralizes the formed acids and has a high reserve alkalinity (ASTM D1121 - 07 Standard Test Method for Reserve Alkalinity of Engine Coolants and Antirusts). The corrosion protection in a contaminated water phase is shown in a corrosion test in accordance to the 14th report of Luxembourg. Additionally MBO acts as hydrogen sulphide scavenger and prevents iron sulphide sludge and sulfide corrosion.

## **CORROSION MITIGATION IN CONTAMINATED FUEL: ACTIVITY OF PIPELINE CORROSION INHIBITORS**

*Matthew Barnes, Ksenija Babic and Joseph Stark*

In order to meet the increasing demands to reduce emissions, manufacturers are designing engines that put greater stress on the fuels being combusted. Consumers are reporting fouling issues associated with injectors and fuel filters when operating diesel engines incorporating the new engine designs. The problems seem to correlate with the fuel contaminants and/or the operational conditions of the injector systems. While there is speculation as to the cause of the deposits being formed, the industry remains uncertain as to the primary contributory factors of the deposits found in new high-pressure common rail engines using ultra-low sulfur diesel fuel.

The primary intention of this study is to shed light on the role of corrosion inhibitors in the formation of internal diesel injector deposits. In addition, to alleviate concerns over these deposits, a new approach towards the development of novel non-acidic corrosion inhibitors is employed. Numerous experiments were conducted, including standard fuel corrosion testing (NACE TM0172), coupled with electrochemical examinations to understand the effects of sodium salts and spent caustic on the performance of corrosion inhibitors in distillate fuel. Filter plugging tests were carried out along with the contaminants previously described to determine the extent of filtration issues in diesel injector systems. The results of this study indicate no negative impact on the effectiveness of the traditional acidic-based corrosion inhibitors, and do not suggest any increase in filter plugging tendency in the fuel along with salt or caustic contamination. Comparative studies with the newly developed non-acidic based corrosion inhibitor show positive trends in inhibitor efficiency and filter plugging tendency.

## **SESSION 9: LONG TERM STORAGE STABILITY OF LIQUID FUELS**

### **ASSESSMENT OF THE EFFECTIVENESS OF ANTIOXIDANT ADDITIONS TO JET A FUEL DOWNSTREAM AT POINT OF USE**

*Janet M. Hughes, Robert E. Morris, Nathan J. Begue, and Kristina M. Myers*

The question of whether Jet A can be used as a “drop in” replacement for MIL-Spec JP-8 fuel in military tactical platforms was investigated. Since commercial Jet-A does not contain any antioxidants, the focus of this work was to determine if Jet A fuel stability could be mediated appropriately by adding an approved antioxidant (AO) to purchased product downstream in the supply chain. In order to make an educated decision regarding the substitution of Jet A for JP-8, two issues had to be resolved. The first was to understand the extent to which antioxidant-free hydrotreated Jet A fuels tend to undergo autoxidative degradation in the supply chain. The second issue was to determine the relative effectiveness of adding approved antioxidants to a reactive Jet fuel at the refinery vs. adding the antioxidant after the fuel has undergone autoxidative degradation in the supply chain or during extended storage. Twenty-two Jet A samples, some with and without antioxidant, were stressed in a low-pressure reactor (LPR) at 90°C and 100 psig O<sub>2</sub> for 24, 48, and 96 hours. Autoxidation during this stress was monitored by measuring hydroperoxide concentrations and antioxidant consumption. It was found that all Jet-A fuels samples tested in the LPR under these conditions were storage stable for up to 16 hours stress time, which is generally considered to predict roughly two years of ambient storage. However, a review of the origins of this correlation in the literature, in addition to our findings obtained under different LPR test conditions, have placed into question the applicability of such accelerated stress testing to predict storage stability of reactive fuels. There was also evidence that addition of the JP-8 additive package (corrosion inhibitor, fuel system icing inhibitor, static dissipater additive) served to increase the extent of autoxidation of these fuels in the LPR.

## **REACTIVE SULFUR MANAGEMENT IN PETROLEUM STORAGE FACILITIES**

*Joseph Stark, Jennifer Draper and Nadjmeh Doostdar*

Hydrogen sulfide (H<sub>2</sub>S) is a naturally occurring gas contained in many of the world's crude oils. It is also formed in the refining process by the degradation of sulfur compounds in crude at high temperatures. Heavy oils, including crude oil, residual fuel and gas oil, therefore tend to have large concentrations of H<sub>2</sub>S. This becomes a concern if these products are to be stored for an extended period or transported. Heavy fuels with high concentrations of hydrogen sulfide can cause corrosion in storage tanks; moreover, these fuels are dangerous to handle and can create odor problems. Thus many refineries, terminals and transport facilities have implemented H<sub>2</sub>S specifications to manage the risks hydrogen sulfide poses to their facility and the surrounding community. Failure to meet these specifications can be costly in terms of personnel safety, delayed or missed shipments and tying up valuable storage tanks. A common way to reduce H<sub>2</sub>S and mitigate its risks is through the use of chemical scavengers that remove hydrogen sulfide from petroleum products. These additives react irreversibly with hydrogen sulfide to form thermally stable reaction products that reduce the hazards associated with hydrogen sulfide. While a variety of products that reduce H<sub>2</sub>S are commercially available, understanding what factors are critical to the success of a specific application is of obvious importance. Temperature, residence time, mixing, and downstream processes are among variables which will affect the additive choice in an application. Investigating these factors is essential to the process of product selection and application optimization. This presentation discusses the selection and application of H<sub>2</sub>S scavengers as well as the other chemical mitigation techniques available to scavenge hydrogen sulfide from heavy oils. These mitigation strategies can also be applied to the storage and handling of other feedstocks and intermediates high in hydrogen sulfide content.

## **CREATING AND MAINTAINING NATIONAL STOCKS AND STRATEGIC RESERVES**

*Dr. Arkadiusz Majoch*

The problem of creating and maintaining national stocks and strategic reserves is one of the most important, in special circumstances, when it becomes necessary to consider seeking to maintain the highest level of diversification of energy resources and security of supply. Although the problem of long-term storage of energy carriers (fuels) is not new, it is still going on legislative path, technical and technological developments aimed at adapting the existing state of the market demand. An element of this is to adapt production technology to use for fuel supplies and provisions. In this paper, it describes the status and trends of the Polish system in relation to European conditions. However, the main component is presentation of the results of five years' storage of motor fuels in model conditions and the use of research results to study on mechanism of chemical degradation of these products during storage.

## **MEASUREMENT OF TRACE ELEMENTS IN PROCESSED FUEL OILS PRODUCED FROM RECYCLED LUBRICATING OILS**

*Dr. Jim Crighton*

Recycling of waste hydrocarbon materials such as used lubricating oils can provide significant benefits in terms of reductions in volumes of waste materials, potentially giving rise to improvements in carbon footprint. However, uncertainty over the point at which the recycled materials cease to be 'waste' as defined in the EU Waste Framework Directive (2008/98/EC) has in some cases inhibited development and marketing of materials which could beneficially be used without damaging human health and the environment. In order to resolve this problem for Processed Fuel Oils produced from recycled lubricating oils, the UK Environment Agency has developed a Quality Protocol which defines the criteria by which used lubricating oils cease to be classified 'waste' following reprocessing. Included in the Quality Protocol are specifications for maximum concentrations of thirteen metals with limits down to 5 mg/kg. However, not all of the metals specified in the Quality Protocol could be measured in these materials at the required levels using existing Standard Test Methods. Due to the urgent requirement for test methods to support the new Quality Protocol, the UK Environment Agency contracted the Energy Institute to evaluate and develop new test methods suitable for inclusion in the Protocol. The residual type PFOs (currently the most commonly produced), present particular analytical challenges in view of the inhomogeneous nature of the samples and the fact that many of the metals are present in the samples in the form of particulates. The analytical challenges are compounded by the requirement to measure potentially volatile elements such as Hg, As and Tl which are easily 'lost' during the ashing step typically used in conventional test methods for determination of metals in this type of sample (e.g. IP 501). This poster will describe the development of three new Standard Test Methods for measuring trace elements in residual PFOs. IP 592 and IP 593 for measurement of Pb, Ni, Cr, Cu, Zn, As, Cd, Tl, Sb, Co, Mn and V using microwave digestion ICP-MS and WDXRF respectively; and IP 594 for determination of Hg using combustion, amalgamation, cold vapour atomic absorption spectrometry (CVAAS).. The relationship between the methods and comparisons with traditional approaches such as IP 501 will also be discussed. The complete project from initiation, ruggedness trail, inter-laboratory study and publication of the final methods was completed in less than one year.

### **John D. Bacha Student Award Paper:**

#### **THERMAL OXIDATIVE STABILITY OF MIDDLE DISTILLATE FUELS – PART 1: CHEMISTRY OF DEPOSIT FORMATION**

*Christopher G. Kabana, Victor Fiorina, Colin Schmucker, Bruce Beaver*

The Soluble Macromolecular Oxidatively Reactive Species (SMORS) hypothesis proposed by Hardy and Wechter(1) for the oxidative degradation of diesel fuels has recently been applied to describe jet fuel oxidative degradation(2). The present work entails a carefully designed dopant study to determine the effect of model SMORS doping on a jet fuel. It has been determined that oligomers that could form through the SMORS mechanism can lead to an increased amount of oxidation. In addition, the SMORS experimental protocol is applied to commercial Ultra Low Sulfur Diesel (USLD), with interesting results.

## **SESSION 10: FUEL MICROBIOLOGY**

### **CAN NON-CHEMICAL ANTIMICROBIAL DEVICES REPLACE OR AUGMENT FUEL TREATMENT MICROBICIDES?**

*Frederick J. Passman, PhD, Gerald L. Munson, and Robert E. Kauffman*

Despite their history of successful use as fuel system disinfectants and fuel preservatives, antimicrobial pesticide use faces increasing restrictions due to both regulatory control and public concerns. A variety of non-chemical treatments have been used with varying degrees of success to disinfect non-fuel fluids and to at least partially inhibit biofilm development on infrastructure surfaces. Promoters of one technology have claimed successful fuel disinfection and fuel-tank fouling prevention. This paper will review a range of non-chemical treatment technologies and will present the results of preliminary evaluations of several technologies that were tested on Jet A fuels that had been challenged with either *Pseudomonas aeruginosa* or *Hormoconis resiniae*. Data are presented on treatment impact on adenosine triphosphate (ATP) concentration, culturability and live/dead direct counts in Jet A-1 and on glass microcosm surfaces. This work was supported by USAF SBIR Research Grant FA8656-10-M-2034.

### **A COMPARISON STUDY OF THE EFFECTS OF BACTERIA CONTAMINATION ON ALTERNATIVE FUELS VERSUS PETROLEUM-DERIVED FUELS**

*Susan Mueller, Oscar Ruiz, Ellen Strobel, Loryn Bowen, Marlin Vangsness, Lisa Brown, Lori Balster Steven Zabarnick and Nicholas Brown*

The University of Dayton Research Institute in conjunction with the United States Air Force Research Laboratory conducted microbiological testing on a variety of alternative fuels to compare the effects of bacterial contamination on the newer fuels with the effects seen in petroleum-derived fuels. Known fuel microbes were added to the fuels, and the fuels were then monitored for a period of 42 days. Tests used to monitor the changes in the fuel included Adenosine triphosphate (ATP) levels and Real-Time Polymerase Chain Reaction (RT-PCR) for bacterial growth levels.

### **ADVANCES IN MICROBIAL MITIGATION OF AVIATION FUELS**

*Oscar N Ruiz*

Microbial colonization of conventional and alternative aviation fuels presents a real concern to military and civil aviation because it can negatively impact fuel quality by degrading fuel hydrocarbons and additives. Furthermore, extensive microbial growth and biofilm formation can lead to costly and disruptive damage to fuel systems and aircraft hardware. Currently, there is no simple, low cost, and effective mechanism to protect fuel against the harmful effects of microorganisms. Because of this, the evaluation of safe, easy to use, and cost-effective methods to prevent, control and even remediate microbial fuel contamination is of utmost importance. Here we discuss a two-prong approach to prevent and mitigate microbial growth and its adverse effects. First, we discuss the development of molecular methodologies that allow rapid detection, quantification, and risk assessment of microbial contamination in fuel. The use of these

molecular technologies to monitor the progress of microbial contamination and to assess the risks related with certain types of fuel-degrading microorganisms can greatly reduce the costs associated with prevention and remediation of microbial fuel contamination. The second approach entails the evaluation of new biocide and biostatic agents, including peptides, nanomaterials, and small molecules that show strong inhibition of vegetative growth and biofilm formation while being easy to use, cost-effective, and safe. It is expected that these new antimicrobial agents will be required in very low concentrations to inhibit microbial growth in both conventional and alternative aviation fuels. By combining better risk assessment and microbial characterization with novel antimicrobial materials we can ensure fuel integrity while decreasing costs and safety concerns in aviation. 88ABW-2011-0028.

### **BIOLUMINESCENCE RESPONSE TO MICROBIAL FUEL CONTAMINATION IN THE LABORATORY AND IN THE FIELD**

*Marlin Vangness, Charlotte Lindhardt and Edward W. English, II*

Over the past several decades bioluminescence has evolved from a novel and detail-oriented laboratory procedure to a rapid assay system that can be surprisingly portable and performed with minimum training. It is possible that, utilizing specific testing platforms, has led to new and innovative ways to verify signal response in difficult sample matrices, reduce sample test volumes, and expand the repertoire of microbial testing. This paper will discuss a number of new and novel techniques that enhance microbial testing and important information without creating an excess burden on the user.

### **MONITORING OF EFFECTIVITY OF BIOCIDES DURING STORAGE SIMULATION OF DIESEL (B0), BIODIESEL (B100) AND BLENDS (B7 AND B10)**

*Zimmer, A.R., Cazarolli, J.; Bento, F.M.; Teixeira, R. M.; Viscardi, S.L.C.; Cavalcanti, E. S. H.*

Microorganisms are a cause of many operational problems (specially filter plugging) during storage and handling oil systems. The susceptibility of diesel systems to microbial contamination has been studied for many years and the addition of biodiesel (Brazil- B5) brought different conditions to the tanks around the world. The goal was the evaluation of two biocides (A- soluble in oil and water phase) and B (additive as multifunctional package, soluble in oil phase) in biodiesel (B100 - 70% soya and 30% tallow); conventional diesel (B0- low sulfur 50ppm) and its blends B7 and B10. The effectivity of two biocides (at 400 and 1000 ppm) was determined by evaluating the changes in a set of parameters during the course of 60-days exposure to an uncharacterized mixed microbial inoculums. Microcosms (200 mL glass flasks) contained fuel and two types of water phase: bottom-water from B5 storage tank or a synthetic water and three levels of contamination CFU.mL<sup>-1</sup>, low (10<sup>2</sup>-10<sup>3</sup>); media 10<sup>5</sup> and e high 10<sup>9</sup>. Fuel as received with water phase without biocide was used as a control and the sampling times were at 0, 7,14,21,42 e 60 days. The fuel phase was rated for Haze scale (ASTMD 4176) and infrared analysis. Water phase parameters included: microbial viability (time kill), pH, presence of emulsion/biofilm and the biomass formed at interface (dry weight). The results suggest that the biocide B (400 and 1000 ppm) can control microbial population just when the microbial

contamination level is low. The presence of biodiesel increased the biomass and the antimicrobial strategies must be considered.

## **SUSTAINABLE AND EFFECTIVE PRESERVATION STRATEGIES FOR ULTRA LOW SULFUR DIESEL, BIODIESEL, AND UNLEADED GASOLINE**

*Beth Ann Browne, Ph.D.*

Many species of bacteria, mold, and yeast have the ability to utilize hydrocarbons in fuel as their sole carbon source for growth. Bacterial and fungal contamination negatively impacts fuel performance properties, such as efficiency and stability, and may increase the frequency of machinery malfunction, engine failures, aircraft gauge malfunction, and impaired water removal from storage tanks. Optimized biocide usage is critical to the fuel industry to maintain the integrity of fuels at all points during storage, distribution, and usage to prevent unnecessary disposal of valuable fuel products. Microbial challenge test data will be presented to demonstrate effective usage of several biocidal chemistries for protection against fuel spoilage by the industrially relevant organisms *Pseudomonas aeruginosa* (bacterium), *Hormoconis resinae* (filamentous fungus), and *Yarrowia tropicalis* (yeast). Effective dosing strategies (maintenance versus shock treatments) will be discussed along with steps for prevention of fuel spoilage. A holistic strategy on sustainable practices will be presented which includes comparisons of environmental and toxicological data for a variety of fuel preservation products.

## **POSTER SESSION**

### **MAGNETIC FILTRATION – A PIPE-LINE TRIAL**

*Alisdair Q Clark*

The Aviation Industry strive to ensure fuel delivered to aircraft is of the highest quality through the elimination of dirt and water at various points along the distribution chain. This paper focuses on one of those points, product exiting a pipe-line to enter intermediate storage for recertification before onward shipment to a major airport. Both traditional and novel analytical techniques are used to examine the trace dirt and water present in the system with some surprising results. Standard filtration systems and overhaul procedures are then presented followed by the design and installation of a magnetic filter. Detailed analysis of the magnetic unit is provided covering health/safety assessment, ergonomics, rate of rust capture, loading, particle size distribution and reduction in environmental waste. In conclusion the benefits and limitations of magnetic versus traditional filtration are summarised.

### **COMPARISON OF NEAT AND WORST-CASE FAME CONTAMINATED AVIATION TURBINE FUEL**

*Pamela M. Serino*

FAME (Fatty Acid Methyl Esters) is the primary source of alternative/renewable fuels for non-aviation applications. In typical applications it is used at blend levels between 5-20% in

conventional diesel fuels. Up until recently most of the blending took place at supply terminals before delivery to the final customer. That model is not sustainable due to the regulatory demands for increased volumes of renewable fuels that far exceed terminal blending capacity. In addition, many specification authorities are adopting 'no-report' limits, such as the 5% in ASTM D975, that allow diesel fuel containing FAME to be transported without special notice.

Currently, jet fuel is not allowed to be contaminated with FAME. FAME contaminations have already occurred in Europe where the regulatory demand has already forced diesel fuels containing up to 7% FAME into the common transport system. A 5 mg/kg contamination limit is at the threshold of detection for FAME and was adopted on the basis that 'none' is not a rational value for analysis. There are waiver programs for emergency situations (for up to 30 mg/kg) but there is a desire for a more reasonable limit for 'no-harm' contamination. The current goal is to allow up to 100 mg/kg without any special requirements. To pursue this goal there is an aviation industry wide consortium, coordinated by the Energy Institute (EI) of the United Kingdom. This program, while associated in practice, is actually a separately funded evaluation by DLA Energy, an arm of the U.S. Department of Defense. While the EI program has conducted a significant amount of physical property testing, most of that was done with a blend of the four most common FAME types. Some observers question whether that approach does not naturally cancel some effects of specific family types. The DLA Energy program thus was intended to evaluate the effect of a single statistical worst-case FAME.

## **NOVEL APPROACHES TO ENHANCED FUEL STABILITY: POLYMER SUPPORTED ANTIOXIDANT SYSTEMS**

*David J. Evans, Paul M. Rawson and Renee Webster*

The Australian Defence Force stores middle distillate fuels in a range of environments for extended periods. To guard against premature degradation and to extend storage life in remote locations we have developed several new polymer supported antioxidant systems that can be modified for inclusion into storage tanks. These polymers supported antioxidant systems retard the oxidation process without additional dosing of the fuel with more additives. Prior to these polymer supported antioxidant systems we have trialled fuel stability foam. These foams have effectively increased the stability of diesel fuels however this is not the case with aviation fuels. We have demonstrated that the fuel stability foam has a detrimental effect on aviation fuel stability which we have previously measured using peroxide values and sediment/gum formation. We have synthesised a new range of polymer supported additives and evaluated them in controlled laboratory experiments using a PetroOxy rapid small scale oxidation tester. The fuels are tested with a range of polymer supported antioxidants at varying concentrations by heating a sample to 140 °C with an initial overpressure of 700 kPa until a 10% pressure drop is achieved, viz. induction period (ASTM D7545). Initial studies show that the induction period of a commercial diesel fuel can be increased from 1 hour 41 minutes to 7 hours 19 minutes. Additionally, the metal deactivating properties of some of the synthesised polymer supported antioxidants has also been successfully examined with copper being coordinated onto the polymer from an AVTUR sample containing 5 ppm of copper ions.



## **A NOVEL QUALITATIVE TECHNIQUE FOR THE IDENTIFICATION OF N,N'-DISALICYLIDENE-1,2-PROPYLENEDIAMINE (MDA) IN AVIATION FUELS.**

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

Additive packages to enhance aviation fuel storage and thermal stability incorporate many compounds to inhibit oxidation. In order to control the catalytic effect free metal ions play in oxidation N,N'-disalicylidene-1,2-propylenediamine may be added as a metal deactivator additive (MDA) by the refiner. A thermal stability additive, NATO designation S-1749, also contains MDA as an integral component. Silica doped with copper or nickel has been utilised to establish a rapid qualitative method to determine if a fuel contains MDA. The use of copper doped silica results in the formation of a vivid purple band in the silica gel which is easily identified. Fourier Transform Infrared (FT-IR) confirms the formation of a [Cu(MDA)] complex with  $\nu$  (C-O) stretching occurring at 1314 cm<sup>-1</sup>, a shift of 43 cm<sup>-1</sup> from the free ligand. This colourimetric method utilises simple techniques without the use of expensive laboratory equipment and has provided detection down to 0.5 ppm. The method was suitable as a field technique as it requires only the test tube and a disposable syringe.

## **HYDROGEN SULFIDE DIFFUSION IN JET FUELS AND ITS FATE DURING FUEL TRANSPORTATION AND STORAGE**

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

Israeli jet fuel, conforming to all specification requirements, became corrosive, several times, to copper strip during transport through a pipeline. The same phenomenon was observed twice, as well, following transfer of jet fuel between storage tanks. A thorough investigation showed that the fuel was corrosive to silver strip as per IP 227 prior to shift from one location to another. From previous studies it is known that the silver strip corrosion test is more sensitive to the presence of hydrogen sulfide while the copper strip corrosion test as per ASTM D 130 is more sensitive to the presence of free sulfur in the jet fuel. Hydrogen sulfide can be found in jet fuel as a result of insufficient stripping after hydrogenation or due to liberation by Sulfate Reducing Bacteria in stagnant water bottoms of storage tanks. The US Standard specification for Aviation Turbine fuels ASTM D-1655 and US Military Specifications Mil-T 83133 stipulate compliance with the copper strip test only. The silver strip corrosion test was mandatory in the British specification DERD 2494 until 2005. The test was suspended on the ground that modern aircrafts are no more equipped with pumps fitted with silver plated slipper pads. In view of the results obtained in this study, jet fuel, meeting specification requirements, may become corrosive to copper strip during transfer through a pipeline or from one storage tank to another due to oxidation of hydrogen sulfide to elemental sulfur. In our opinion some thought should be given to reinstatement of silver strip corrosion test in international jet fuel specifications. Silver strip corrosion test has been already incorporated in Israeli jet fuel specification No 5563 as a reliable tool for disclosure of hydrogen sulfide presence in jet fuel.

## **MATH-CHEMICAL ADJUSTMENT OF THE INDEXES RON AND MON OF GASOLINE COMPONENTS HYDROCARBONS**

*César Pernalete, César D. Barreto, Ayni G. Sanchez, Lolibeth J. Quijada, Marien C. Rojas, Franklin J. Romero*

In order to have a database with the octane number values RON and MON, for a wide variety of gasoline components, a criterion has been presented for the adjustment of these indexes from the determination of different kinds of individual hydrocarbons by high resolution gas chromatography. A polynomial correlation was applied, setting the octane number as a function of carbon number in each chain of hydrocarbon families. For a family of molecules, the octane number decrease with an increment in the chain length, so this criterion was used to validate every index adjustment. The equations obtained by these correlations were validated through of an analysis of variance (ANOVA), obtaining a second order polynomial equation with a decreasing trend. The adjusted values were compared with results of method ASTM D2700 and ASTM D2699, obtaining considerable similitude between both results. This work incorporates the empirical nature of the RON and MON values with the theoretical behaviors observed with the increase in the chain length.

## **FLASH POINT PREDICTIONS FOR FUEL COMPOUNDS USING QSPR METHODS**

*Diego Saldana, Benoit Creton, Pascal Mouglin, Laurie Starck, Ludivine Pidol, Nicolas Jeuland, Bernard Rousseau*

Alternative fuels, such as Fischer-Tropsch, Hydrotreated Vegetable Oils and Fatty Acid Esters are currently being explored as a way to reduce greenhouse gas emissions for the aircraft and/or automotive sectors. Alternative fuels must be compatible with engines that are currently available on the market, which is why it is necessary to make sure that candidate fuel formulations satisfy a number of requirements. Concurrently, it is necessary to develop a rational approach to mixture component selection. This work aims to develop a new methodology to optimize alternative fuel formulation by using statistical learning models to find the best suited composition in terms of several properties that are included in the specifications. Properties modelled in this study include Flash Point, Cetane Number, Viscosity and Density estimation. Our databases include hydrocarbons such as normal and iso-paraffins, olefins, naphthenes and aromatic compounds, as well as oxygenated molecules, including alcohols and esters. We will compare the results of different combinations of predictive methods, predictor variables as well as the type of validation used for optimizing model parameters. Non-linear models are known to be potentially more accurate but difficult to reverse, whereas linear models can be less accurate but more easily reversible. Our aim is to combine the accuracy of non-linear models with the reversibility of linear models, effectively establishing a Computer Aided Molecular Design methodology. This kind of predictive approach will allow to anticipate the behaviour and improve the quality of future fuel blends, including alternative fuels.

## **FUEL LONG-TERM STORAGE STABILITY EVALUATED BY MIDDLY ACCELERATED TEST CONDITIONS**

*Mickaël Sicard, Bruno Raepsaet, Jacques Ancelle and Frédéric Ser*

European ALFA-BIRD (ALternative Fuels And BIOfuels for aiRcraft Development) program aims at developing the use of alternative fuels in aeronautics. During this program, the most promising solutions are examined and detailed analysis performed on the selected fuels. A lot of properties have to be considered to determine the potentiality of a new fuel. Storage stability is one of the issues. To determine the long-term behavior of the fuels, the ASTM D 4625 procedure is used. The fuel is stored during several weeks at 43 °C. According to the procedure, the fuel aging results "in an approximately fourfold acceleration of the degradation for an ambient temperature of 21 °C, that is, a week of 43 °C storage is roughly equivalent to a month of storage at normal (environmental) ambient temperature. The long-term stability of the four ALFA-BIRD fuels (a CtL, a GtL, a blend 50 % GtL +50 % naphtenic cut and a blend 80 % GtL + 20 % hexanol) and a Jet A-1, used as reference, is evaluated. Besides the 43 °C temperature advised in the ASTM procedure, the influence of two additional temperatures (-40 and 20 °C) and the influence of humidity at 20 °C are also determined. Fuels are aged for period of 0, 4, 8 12, 24 weeks and 1 year. The samples are characterized by various analytical techniques (FTIR, GC, HPLC, particle counting...) in order to evaluate the evolution of the liquid phase in function of the storage length. For the 5 fuels, no visible modification (solution color, suspended particle) is observed. In the same way, it is not possible to highlight difference between the initial liquid phase and after storage. Thus, the conclusion is simple: the tested fuels seem to be perfectly stable under long –term storage conditions (4 years simulated).

## **A RAMAN-BASED PORTABLE FUEL ANALYZER**

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Fuel is the single most import supply during war. Consider that the US Military is employing over 25,000 vehicles in Iraq and Afghanistan. Most fuel is obtained locally, and must be characterized to ensure proper operation of these vehicles. Fuel properties are currently determined using a deployed chemical laboratory. Unfortunately, each sample requires in excess of 6 hours to characterize. To overcome this limitation, we have developed a portable fuel analyzer capable of determine 7 fuel properties that allow determining fuel usage. The analyzer uses Raman spectroscopy to measure the fuel samples without preparation in 2 minutes. The challenge, however, is that as distilled fractions of crude oil, all fuels are composed of hundreds of hydrocarbon components that boil at similar temperatures, and performance properties cannot be simply correlated to a single component, and certainly not to specific Raman peaks. To meet this challenge, we measured over 1000 diesel and jet fuels from around the world and used chemometrics to correlate the Raman spectra to fuel properties. Critical to the success of this approach is laser excitation at 1064 nm to avoid fluorescence interference (many fuels fluoresce) and a rugged interferometer that provides 0.1 cm<sup>-1</sup> wavenumber (x-axis) accuracy to guarantee accurate correlations. Here we describe the portable fuel analyzer, the chemometric models, and the successful determination of these 7 fuel properties for over 100 unknown samples provided by the US Marine Corps, US Navy, and US Army.

## **PROPERTIES OF GASOLINE AND DIESEL FUELS CONTAINING RENEWABLE DROP-IN BIOFUEL BLEND STOCKS PREPARED BY THE THERMO-CATALYTIC CONVERSION OF LIGNOCELLULOSE**

*Vicente Sanchez, Leslie May, John Kasbaum, Dan Strope, Ph.D., and Jeff Trewella, Ph.D.*

The liquid transportation fuels market is the largest market in the world, representing over \$2 trillion in revenues on a global basis. Key products are gasoline, diesel fuel, jet fuel and fuel oil for railroad and marine applications. Each of these finished products is produced by blending together a variety of blendstocks produced in refineries. These blends are then supplemented with a variety of additives designed to overcome deficiencies (e.g. antioxidants) or impart added benefits (e.g. detergency). In the US, the market for renewable fuels is stimulated by the Renewable Fuel Standards, RFS1 and RFS2. Combined, these standards correspond to a US market of over \$100 billion. Key products under RFS2 are gasoline and diesel fuel blendstocks that are derived from non- petroleum, renewable sources. This poster will present the results of studies aimed at evaluating the product quality aspects of fuels containing renewable blendstocks. Data will be shown illustrating that finished fuels containing oil produced by the thermo catalytic conversion of lignocelluloses feedstock meet ASTM standards for gasoline and diesel fuel.

## **MONITORING OF EFFECTIVITY OF BIOCIDES DURING STORAGE SIMULATION OF DIESEL (B0), BIODIESEL (B100) AND BLENDS (B7 AND B10)**

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Microorganisms are a cause of many operational problems (specially filter plugging) during storage and handling oil systems. The susceptibility of diesel systems to microbial contamination has been studied for many years and the addition of biodiesel (Brazil- B5) brought different conditions to the tanks around the world. The goal was the evaluation of two biocides (A- soluble in oil and water phase) and B (additive as multifunctional package, soluble in oil phase) in biodiesel (B100 - 70% soya and 30% tallow); conventional diesel (B0- low sulfur 50ppm) and its blends B7 and B10. The effectivity of two biocides (at 400 and 1000 ppm) was determined by evaluating the changes in a set of parameters during the course of 60-days exposure to an uncharacterized mixed microbial inoculums. Microcosms (200 mL glass flasks) contained fuel and two types of water phase: bottom-water from B5 storage tank or a synthetic water and three levels of contamination CFU.mL<sup>-1</sup>, low (10<sup>2</sup>-10<sup>3</sup>); media 10<sup>5</sup> and e high 10<sup>9</sup>. Fuel as received with water phase without biocide was used as a control and the sampling times were at 0, 7,14,21,42 e 60 days. The fuel phase was rated for Haze scale (ASTMD 4176) and infrared analysis. Water phase parameters included: microbial viability (time kill), pH, presence of emulsion/biofilm and the biomass formed at interface (dry weight). The results suggest that the biocide B (400 and 1000 ppm) can control microbial population just when the microbial contamination level is low. The presence of biodiesel increased the biomass and the antimicrobial strategies must be considered.

## **SIMPLIFIED METHODOLOGY FOR DETERMINING STABILITY IN MIXTURES OF CRUDE OILS**

*Luciano Messina Stor*

Studies on colloidal properties of asphaltenes are motivated by their propensity to aggregate, flocculate, precipitate and be adsorbed on surfaces. The tendency of asphaltenes to participate in colloidal and interfacial phenomena, despite being a well-known problem, still demands high costs in the oil industry. There are different methodologies for predicting the stability of mixtures of oils or finished petroleum products, where the asphaltene precipitation issues are also important, as, e.g., the mix of industrial and marine fuel oil (bunker). These methodologies, intended to predict the future behavior of a given mixture, are usually very complex and provide unreliable results for some oils where most of them have been developed for oils with high asphaltenes content. The main objective of this study is to evaluate a new methodology to predict the behavior of crude oil mixtures by using stability parameters readily obtained from product's specification without any additional laboratory test. This new methodology named IFST (Farah Stor Total Index) is based on density (API gravity) and viscosity (A and B parameters from Walther-ASTM equation) and is designed to evaluate the stability behavior of a single or blending of crude oils. The stability parameters from IFST methodology are given below.

### Stability control of the IFST

IFST > 38	Stable
30 < IFST < 38	Poor Stability
22 < IFST < 30	High Risk of Instability
IFST < 22	Unstable

## **ALTERNATIVE JET FUELS – TURBINE ENGINE EMISSIONS CHARACTERISTICS**

*Edwin Corporan, Matthew J. DeWitt, Christopher D. Klingshirn, David Anneken and Richard Striebich*

Over the past decade, the US Air Force has been collaborating with manufacturers of alternative (non-petroleum) jet fuels to assess the potential of these fuels for use in military weapon systems. The Air Force Research Laboratory (AFRL) in collaboration with the University of Dayton Research Institute (UDRI) have been extensively evaluating the chemical and physical characteristics, as well as fit-for-purpose properties and engine emissions of these alternative fuel candidates to ensure system compatibility and assess environmental impact. It has been consistently demonstrated in a variety of turbine engine platforms that significantly lower smoke, i.e. particulate matter (soot), is produced during operation with Fischer-Tropsch (FT) derived Synthetic Paraffinic Kerosene (SPK) or Hydroprocessed Renewable Jet (HRJ) fuels and blends. This is primarily the result of the low concentration or absence of aromatic compounds in the alternative fuel. Several engines have also shown significantly lower unburned hydrocarbons, carbon monoxide and hazardous air pollutant (HAPs) emissions with the alternative fuels. In this effort, the emissions performance of recently tested engines operated on alternative fuels are studied and compared. Potential correlations of the emissions behavior with engine type, fuel

properties and operating conditions are explored. The platforms studied include two turboshaft (T63 & T701C) and four turbofan (CFM56, F117, TF33 and PW308) type engines.

## **OVERVIEW OF EFFORTS TO DETERMINE MINIMUM REQUIRED FSII USE AND PROCUREMENT LIMITS FOR USAF AIRCRAFT**

*Matthew J. DeWitt, Steven Zabarnick, Theodore Williams, Zachary West, Linda Shafer, Richard Striebich, Scott Breitfield Ryan Adams, Rhonda Cook, Charles L. Delaney and Donald Phelps*

There is significant interest in determining if the on-board aircraft use concentration of the Fuel System Icing Inhibitor (FSII) additive required in U.S. military aviation fuel JP-8 (currently 0.07% DiEGME by volume) can be reduced. The primary function of the FSII is to prevent solidification of free water within the fuel, which can adversely affect fuel system operation. A reduced FSII concentration will yield significant logistical and economic cost savings and possibly reduce the occurrence of undesirable material compatibility issues attributed to DiEGME. An extensive research program was performed to provide improved insight into the manner by which FSII interacts with free and dissolved water and prevents ice formation in fuel systems. These efforts have provided valuable insight for the determination of a minimum FSII use limit which will maintain comparable anti-icing and biostatic performance to that for current specification levels. Several of the efforts in this program were presented and discussed at the 10th and 11th International IASH Conferences; additional results and progress, including recommendations for the reduced FSII use and procurement limits will be presented in the poster.

## **THE U.S. AIR FORCE'S ASSURED AEROSPACE FUELS RESEARCH FACILITY FISCHER-TROPSCH LIQUIDS UPGRADING REACTOR**

*Heinz J. Robota, Russell K. Smith, Robert W. Morris Jr.*

As part of a strategic initiative to prepare for the broader use of synthetic aviation fuels, the United States Air Force is constructing a facility which will allow it to produce synthetic aviation fuels and fuel components in quantities sufficient for small scale engine testing. When completed, it will be possible to produce synthesis gas, convert synthesis gas to liquids, and further process these liquids to fuel and fuel components which can be separated by distillation. Here we describe the operation of a catalytic hydrocracker for the conversion of normal alkane feedstocks to jet fuel as the first phase of this effort. The unit is designed to produce in the range of 10-15 gallons of jet fuel per day. A commercially available cut of a Fischer-Tropsch wax with carbon numbers ranging from about C20 to C60 and a distribution peak in the C30-C35 range, serves as the initial test feed. This broad distribution of paraffins is isomerized and hydrocracked over a commercially manufactured, unsulfided, Co/MoO<sub>3</sub>/Silica-Alumina catalyst to yield naphtha and fuel fractions which are subsequently isolated in a fractionator and vacuum distillation column, respectively. The insufficiently converted distribution left in the vacuum bottoms is then recycled to the entrance of the catalytic cracking unit where it is continuously combined with fresh feed. We describe the initial operating characteristics, cracking, and product recovery results.

## **THE EFFECT OF AROMATIC TYPE ON THE VOLUME SWELL OF NITRILE RUBBER IN SELECTED SYNTHETIC PARAFFINIC KEROSENES**

*John Graham, Donald Minus, and Timothy Edwards*

A barrier impeding the full adoption of synthetic paraffinic kerosenes (SPKs) as alternative fuels is concerns with their material compatibility. As-produced SPKs are composed of normal, branched, and cyclic paraffins resulting in fuels that are very inert with respect to their interactions with polymers. This contrasts with conventional fuels which can show significant solvent character in the form of swelling and softening polymeric fuel system materials. There is concern that exposing materials that have been in service with conventional fuel to an alternative fuel may cause them to shrink, harden and fail. The most acute concern is for O-rings which rely on their size and resiliency to perform their function. The near-term solution is to blend aromatics with the SPKs to increase their solvent character. It is desirable to identify the most effective aromatics that could be used for this purpose. In this study the volume swell of nitrile rubber was measured using 6 reference JP-8s, 4 SPKs and 11 aromatics. The aromatics were selected to examine the influence of molar volume, polarity, and hydrogen bonding on their performance as swelling promoters. It was found that hydrogen bonding had the largest effect followed by polarity and molar volume. Furthermore, it was found that the same rules apply to the SPK itself with lighter fuels providing a higher baseline volume and this characteristic had a significant effect on the minimum treatment level. Overall, it was found that within the boiling range of jet fuel the individual effects of molar volume and polarity are relatively subtle and the ability to introduce hydrogen bonding is limited. The most effective fuels combine these factors by minimizing molar volume and maximizing polarity and hydrogen bonding.

## **DETERMINATION OF FAME CONTAMINATION IN AVIATION TURBINE FUEL USING GAS CHROMATOGRAPHY**

*L. Spino, E. Barendregt, R. Suijker and R. de Jong*

Blending of Fatty Acid Methyl Ester (FAME) stocks into diesel fuels for automotive use, which is often mandated by governments, holds the potential risk of contaminating jet fuel streams when supply chains are shared. The presence of FAME components leads to small changes in physical properties of the jet fuel, which may result in fuel gelling, line blockage or even engine failure. International jet fuel specification (e.g. DEF STAN 91-91) therefore limits FAME content to less than 5 ppm w/w total FAME. A new analytical method for determining FAME contamination in Jet Fuel streams was developed based on classical deans switching and refocusing. FAME species eluting from the non-polar pre-column are trapped and refocused on the first part of the second-dimension column by using temperature-based trapping before final separation. Flame-ionization detection (FID) and external standard calculation of individual FAME species is used for quantification. Identification of FAME components at sub-ppm level in Jet Fuel matrices is unambiguous with a Retention Time variation of 0.02%. Sensitivity was found to be better than 0.5ppm and 2 mg/kg (w/w) for individual FAME components and total FAME respectively. Repeatability for the method was 2.8% (n=10) at 6.6 ppm w/w total FAME and correlation was better than 0.999 in ranges 1 – 50 mg/kg and 10 - 100 mg/kg (C16:0). A simple and robust analysis technique based on two-dimensional GC has been developed for

determining FAME contamination at ppm level in aviation turbine fuels as specified in DEFSTAN 91-91.

### **A NOVEL NEW MSEP DETERMINATION INSTRUMENT**

*Alan J. Fougere and Ian Mylrea*

D-2 Incorporated along with Stanhope-Seta have developed a new instrument for MSEP determinations consistent with the current ASTM Test Method D3948. The filterability of fuel as represented by a MSEP value was a test originally introduced in the 1970's has recently been plagued with poor repeatability & reproducibility. ASTM inter-laboratory round robin reports the current method had a standard deviation of +/-21 on a test that requires a minimum ready reading of 75 on a scale of 50 -100. The new fully automated sensor and sample handling system that uses a novel differential capacitance detector along with new API 1655 Filter materials has been shown to improve consistency of MSEP results. A detail instrument description along with results shall be presented. An ASTM task force has been formed and current status report on testing and verification from this group will also be presented.

### **AN INNOVATIVE DENSITY MEASUREMENT TECHNOLOGY FOR MONITORING THE QUALITY OF LIQUID AND GASEOUS FUELS**

*Wesley Sund and Rick Smith*

Density measurements have long been used to monitor petroleum distillation. The density of petroleum fractions decrease as one moves up the primary crude distillation column. Today, measuring the density or specific gravity of biodiesel has been reported to be the preferred method of blending biodiesel fuel for both accuracy and ease of use. Instruments for measuring density have been traditionally constructed from metals. For a successful, widespread adoption of a new measurement technology it must not only be capable of accurately measuring a parameter when compared to conventional technology, but it also must do so in a more economical manner. Crystalline silicon micromachined sensors have revolutionized measurements, such as pressure and temperature, by reducing the sensor size and increasing the sensor performance. This poster explores the design and application of silicon based MEMS (MicroElectroMechanical Systems) technology to fuel monitoring, custody transfer, quality control and blending. These microfluidic sensors have on-chip capabilities to measure density / specific gravity, and temperature, which will be demonstrated in the experimental results. The MEMS sensor's ability to differentiate between gasoline, ethanol, diesel, biodiesel, butanol, Fischer-Tropsch fuel, water and air contamination with a density measurement will be demonstrated. Using fluid density, concentrations of fuel blends like ethanol-gasoline can be measured. Contamination levels of water in ethanol can also be measured in this manner. An integrated high accuracy temperature sensor allows the measured density to be corrected to standard conditions, which allows these MEMS sensors to be applied to fluid custody transfer. The low mass MEMS technology has also been applied to gas mixtures, including components such as hydrogen, methane and natural gas, to monitor average molecular weight, specific gravity and heating value. Vibration testing has been undertaken to show that these



micromachined devices, with their high resonant frequencies, are immune to vehicular and aviation vibration, unlike conventional density meters made using larger resonating steel tubing.