

10TH INTERNATIONAL CONFERENCE ON STABILITY, HANDLING AND USE OF LIQUID FUELS

Tucson, Arizona
October 5-11, 2007

Abstract Summaries

SESSION 1: SYNTHETIC FUELS

Keynote Address:

ALTERNATIVE FUELS: WHERE WE ARE AND WHERE WE ARE GOING

Mike Farmery

The paper will examine where the drive for alternative fuels in Aviation is coming from. It will highlight how the relative importance of drivers such as: improving supply diversity, enhancing product performance and mitigation of environmental impact vary from segment to segment. For the key segments of commercial air transport, military and general aviation, current activities and future plans will be summarised. As with automotive fuels, there is particular interest in reducing the CO₂ impact of fuel use and the session will include particular focus on the potential for bio-derived fuels in aviation. The review will cover not only technologies that may be viable in the reasonably short term but also the longer-term ideas that are being proposed and developed around the world. No session on alternative fuels for aviation can fail to mention hydrogen and a very short evaluation will be presented. Simple, straightforward but, above all, interesting questions will be welcome.

COMBUSTION AND OPERATIONAL CHARACTERISTICS OF SASOL FULLY SYNTHETIC JET FUEL

Dr. Clifford A. Moses, Tedd Biddle, Stan Seto, Chris Lewis, Randy Williams, and Piet N. J. Roets

Prior to the introduction of Sasol's semi-synthetic jet fuel (SSJF) at Johannesburg International Airport (JIA) in July 1999, all commercial aviation fuel had been derived solely from petroleum sources. SSJF is a blend of petroleum-derived jet fuel with up to 50 percent of a synthetic iso-paraffinic kerosene (IPK). IPK is processed from synthesis gas through a Fischer-Tropsch process followed by conventional refining processes. Since the approval of SSJF under the DEF STAN 91-91 fuel specification, about half of the jet fuel deliveries to JIA contain IPK in fractions ranging from less than 5 percent up to 50 percent with an average of around 20 percent. SSJF has enabled Sasol to meet the growing demand for jet fuel at JIA despite the limited capacity for petroleum refining in the Johannesburg area. To further ensure future availability, Sasol is now working to develop acceptance of fully synthetic jet fuel from their Fischer-Tropsch process streams. Sasol has 5 process streams in the kerosene boiling range that are synthesized from coal at the refinery in Secunda, South

Africa. These streams are blended appropriately to meet the specification requirements for Jet A-1. In addition, the fuel has been evaluated according to the requirements of DEF STAN 91-91 to demonstrate the fuel is fit-for-purpose as commercial jet fuel. This paper summarizes the engine and combustor tests conducted on Sasol fully synthetic jet fuel to evaluate atomization, ignition and altitude relight, exhaust emissions, and durability. The results of the tests showed that the fully synthetic jet fuel has combustion characteristics that are the same as conventional, petroleum-derived, jet fuel.

EVALUATION OF FISCHER-TROPSCH SYNTHETIC FUELS AS BLENDING STOCKS FOR NAVAL APPLICATIONS

Philip H. Chang and Richard Kamin

Although Fischer-Tropsch (FT) technologies have existed for decades, only recently has the United States Department of Defense begun to look at Fischer-Tropsch derived synthetic liquid fuels for potential military applications. The US Navy evaluated several synthetically derived fuels and their blends with petroleum based JP-5 and F-76 for both potential aircraft and shipboard propulsion applications. In this study, the U.S. Navy tested several FT fuels and their blends against the requirements of the JP-5 and F-76 specifications (MIL-DTL-5624 and MIL-PRF-16884), non-specification area of concern such as storage stability, lubricity, etc. and Petroleum Quality Information System (PQIS) data from Defense Energy Support Center (DESC). Statistical comparisons were made between our test results and values of specifications and past PQIS data. The linear and non-linear properties were identified upon blending with petroleum based fuels. Subsequently, the maximum/minimum allowable blending ratio was determined for FT blends to satisfy the specifications, non-specification and PQIS data.

DOD ASSURED FUELS INITIATIVE: B-52 AIRCRAFT EMISSIONS BURNING A FISCHER-TROPSCH/JP-8 FUEL BLEND

Edwin Corporan, Matthew J. DeWitt, Christopher D. Klingshirn

In support of the DoD Assured Fuels Initiative, the emissions of two TF33 P-103 engines burning JP-8 and a 50/50 blend of JP-8 and Fisher Tropsch (F-T) synthetic fuel were characterized to determine the impacts of the synthetic fuel on the B-52 aircraft emissions. The engines were tested on-wing a parked B-52 aircraft at Edwards AFB, and one of the engines was also tested in Test Cell #8 at Tinker AFB. Measurements of the mostly non-volatile particulate matter (PM) emissions were performed using conventional instrumentation to determine particle number, size, mass and smoke number. Soot samples were collected on quartz filters for subsequent chemical analysis and determination of PM mass via carbon burn-off. Gaseous emissions were also quantified. Both TF33 engines were operated at four power settings, idle-to- maximum thrust, and for the test cell runs, a 50 hour engine endurance test at normal power was also conducted. The PM mass emission indices averaged 1.3 - 4.6 g/kg-fuel for operation on JP- 8 and 0.65 - 3.1 g/kg-fuel for the F-T blend, therefore, reflecting average reductions of 30-50% in PM mass burning the F-T blend relative to JP-8. Significant reductions with the F-T fuel were also observed on particle

numbers and engine smoke numbers. Negligible effects on gaseous products except for reductions in sulfur oxide emissions were observed. Chemical analysis of the soot samples as a function of engine power and fuel, and comparison of on-wing and off-wing engine tests will be presented.

A LABORATORY ASSESSMENT OF THE COMPATIBILITY OF FISCHER-TROPSCH DERIVED (ISO PARAFFINIC KEROSENE) AND BLENDED FT-PETROLEUM-DERIVED FUELS WITH NON-METALLIC MATERIALS

John L. Graham, Richard C. Striebich, Donald K. Minus, William E. Harrison III

Since the synthesis of a liquid hydrocarbon fuel from coal by Franz Fischer and Hans Tropsch in 1923, there has been recurring interest in developing this fuel for military and commercial applications. The Fischer-Tropsch (FT) process can be used to produce high quality liquid transportation fuels from a wide variety of hydrocarbon feedstocks, such as coal, natural gas and biomass, and could reduce reliance on crude oil. FT fuels are unique in that they closely resemble conventional petroleum distillate fuels in their complexity, boiling range, and critical physical properties and they can conceivably be used interchangeably with petroleum derived fuels such as JP-8 and Jet-A. However, a major difference between FT and conventional fuels is that FT fuels are comprised solely of iso- and normal-paraffins and do not contain aromatics and heteroatoms. This is significant in that engine designs and materials have evolved over time to accommodate the idiosyncrasies of petroleum distillate fuels, most notably the interactions between the aromatic components in fuel and non-metallic materials and without these species there may be considerable difficulty in using FT fuels interchangeably with conventional fuels. The present study began by developing a relatively fundamental understanding of how hydrocarbon fuels interact with non-metallic materials, then applying that knowledge to anticipate how alternative fuels such as neat FT and FT fuel blends will interact with these materials. This methodology is proving useful in understanding the fundamental material compatibility issues related to the use of alternative fuels and developing strategies for mitigating these issues. In this paper an overview of the significant results, test procedures, and analysis techniques will be presented.

BLENDED FISCHER-TROPSCH FUELS WITH CONVENTIONAL JET FUELS: THERMAL OXIDATIVE STABILITY

Maria Sobkowiak, Joespha M. Griffith, and Bruce Beaver

The U.S. Air Force has committed to use of 50/50 blends of conventional jet fuels with Fischer-Tropsch fuels by 2016. This paper will exam the thermal oxidative stability, with the ECAT flow rig, of blends derived from a wide range of conventional jet fuels.

SESSION 2: NEW CHALLENGES IN FUEL DISTRIBUTION & STORAGE

THE INTRODUCTION OF ULTRA LOW SULFUR DIESEL FUEL – A SUCCESS STORY

Bradley D. Oberg

The introduction of ultra-low sulfur diesel (ULSD) fuel into the US fuel distribution system in June of 2006 was a much anticipated event. Despite dire predictions of product contamination, fuel shortages, price spikes and market disruptions, the roll out of ULSD has been relatively smooth and quiet. This paper will explore some of the reasons why the big event appears to be a non-event and projects into the future to see if the trend will continue.

INVESTIGATION OF FIELD PROBLEMS CAUSING AIRCRAFT OPERATIONAL ISSUES

Daniel C. Mertens and George R. Wilson, III

In 2005 and 2006 a series of engine start-up incidents involving helicopter operations in a remote location pointed to a problem with the thermal stability of the fuel. A thorough investigation, however, proved the fuel to be adequate for the job and the real problem to lie in how the fuel was handled. In the process of discovering the true causal factors of the situation we learned significant lessons about how individuals jump to conclusions by creating perceptions about a fuel-handling problem in contrast to identifying true, explicit causal factors.

COMMERCIAL MARINE DIESEL FUEL FOR MILITARY APPLICATIONS – RISKS AND RECOMMENDATIONS FOR THE USE OF BIODIESEL AND ULTRA-LOW SULFUR DIESEL FUEL IN TACTICAL EQUIPMENT

Kenneth J. Henz

The military marine distillate fuel specification, MIL-DTL-16884L (F76), provides physical, chemical and performance characteristics of a diesel fuel that can successfully operate engines used in military equipment in marine environments. The US Government procures and stores F76 in deep water terminals either operated by or contracted out by the military. In cases where F76 is not available, commercial marine diesel fuel, refined and blended to commercial specifications, may be purchased from commercial vendors as a substitute. A major chemical property difference between F76 and commercial marine diesel fuel is the requirement for storage stability, essential for F76 but not measured for commercial marine diesel fuel. Commercial automotive diesel fuel could be supplied as marine diesel if the flash point is 60°C or above and meets the remaining commercial marine fuel specification requirements. The Navy could potentially buy this automotive diesel fuel when receiving propulsion fuel at commercial locations through the military bunkers program. Automotive diesel fuels could contain up to 5% B100 Biodiesel with Ultra-Low Sulfur Diesel (ULSD) used as the 95% blending component. This paper provides a literature review of Biodiesel and low sulfur fuels in marine applications and examines their effects on the F76 specification. Recommendations for future study are discussed.

LONG TERM STORAGE OF FUEL OIL IN THE NATURAL GAS ERA

Dr. Josefa Ben- Asher and Sarit Calderon

Environmental requirements caused many energy producing enterprises to switch from fuel oil to natural gas as a principle combustible to accommodate their energy needs. When natural gas is used as an energy source, the burners of the energy-producing units are of the dual kind and can use fuel oil as a combustible when necessary. This is because gas supply is switched off periodically during maintenance of gas pipes or equipment maintenance. The fuel oil is kept in long-term storage close to the working site. This practice guarantees fuel oil supply in case of emergency shut down of natural gas lines. When fuel oil is stored for a long period, deterioration processes can cause operational difficulties when there is a sudden requirement to switch to burning fuel oil. The changes in fuel quality materialize in physical and/or chemical properties. As a result the fuel may not comply with specification requirements nor be compatible with the stipulations of the equipment producer. The paper discusses the possible changes in pour point, water content, ash, and metal content during storage. Chemical changes in the intermolecular relationships of fuel oil, which can change viscosity and stability, are accounted for. Processes connected with fuel oil production causing change in fuel oil stability during long term storage are explained. Finally, recommendations for optimal conditions for fuel oil storage and testing are suggested.

SESSION 3: BIOFUELS I: HANDLING & STABILITY

EFFECT OF BIODIESEL IMPURITIES ON FILTERABILITY AND PHASE SEPARATION FROM BIODIESEL AND BIODIESEL BLENDS

Charley Selvidge

Biodiesel is gaining importance as a complement to the supply of diesel fuel for compression ignition engines. Diesel engines continue to be the dominant source of power for commercial transportation. Because of their superior energy efficiency they are expected to make an even greater contribution in the future with a growing contribution to the enormous passenger car application. Biodiesel is produced by transesterification of natural triglycerides with alcohol, primarily methyl alcohol. The resulting biodiesel product consists of a mixture of compounds primarily the methylesters of the fatty acid moieties in the triglycerides. In addition to the methyl esters, other compounds can be present. Among these is a family of impurities referred to as total glycerin impurities. The total glycerin impurities consist of free glycerin, tri glycerides, diglycerides, and monoglycerides. These are reported as their weight percent based on glycerin content (hence total glycerin). Published biodiesel specifications place a limit on the total glycerin impurities. The phase separation of biodiesel can exhibit time temperature effects that are different from that of typical diesel fuels. These time temperature effects can affect the filtration characteristics of both biodiesel and biodiesel blends. This paper reports experience from field performance and laboratory evaluation of different biodiesel and biodiesel/diesel fuel blends. Differences in performance are related to differences in impurity levels in biodiesel and biodiesel/diesel fuel blends.

ALTERNATIVE FUELS AND MATERIAL COMPATIBILITY

Edward W. English, II

As legislation becomes enacted to reduce green house gases, tail pipe emissions, and our reliance on foreign oil the emerging use of alternative fuels and its impact on the storage and distribution infrastructure is becoming more the topic of interest. Certain materials and strategies once implemented to safely store and distribute petroleum hydrocarbons may now find themselves incompatible as biomass fuels like ethanol blends, ethanol fuel, and biodiesel fuels become more the norm. This shift in fuel strategy from petroleum based fuels to biomass fuels can significantly reshape the way we store and distribute fuels in the future. This presentation will discuss the material compatibility and storage challenges with alternative fuels.

THE RELATIONSHIP BETWEEN BIODIESEL STABILITY INDICATORS AND DEPOSITION TENDENCY, PART 1: COMPARISON OF B100'S OF DIFFERING STABILITY

J. Andrew Waynick, Robert L. McCormick and Steven R. Westbrook

Two soy-based B100's and one used cooking oil-based B100 were evaluated for properties that relate to their stability. These properties included Rancimat induction period, modified D2274 insolubles (total and iso-octane), total acid number (initial and post-D2274), polymer content by size-exclusion chromatography (initial and post-D2274), peroxide value, anisidine value, conjugated diene content, fatty acid methyl ester profile, and viscosity. These three B100's were also evaluated for their tendency to form deposits on a hot steel surface by using the Jet Fuel Thermal Oxidation Tester (JFTOT). JFTOT runs were performed at both 260 C and 300 C, and tube deposit volume was evaluated using ellipsometry. The properties of the three B100's were correlated with the JFTOT deposit volumes to determine which variables appeared to be affecting deposit formation tendency. Also, select properties were measured on the post-JFTOT fuels so as to determine the effect of the hot steel surface stressing on B100 stability-related parameters.

THE RELATIONSHIP BETWEEN BIODIESEL STABILITY INDICATORS AND DEPOSITION TENDENCY, PART 2: EFFECT OF AGING ON STABILITY AND DEPOSITION TENDENCY OF B100'S AND B20'S

J. Andrew Waynick, Robert L. McCormick and Steven R. Westbrook

Two of the three additive-free B100's used in the work previously reported in Part 1 were selected for further investigation. These two B100's, an unusually stable soy-based B100 (Rancimat induction period of 9.1 hours) and a more typical stability soy-based B100 (Rancimat induction period of 5.0 hours) were aged by two procedures: ASTM D2274 stressing and six weeks quiescent aging at 60 C with sealed and non-replenished headspace. B20's were blended using the two B100's and an ultra-low sulfur No. 2 diesel fuel (ULSD). Properties of the two B100's and the two B20's relating to stability were evaluated before and after the aging. The two B100's and two B20's were also evaluated for their tendency to form deposits on a hot steel surface by using the Jet Fuel Thermal Oxidation Stability Tester (JFTOT). JFTOT runs were

performed at both 260 C and 300 C, and tube deposit volume was evaluated using ellipsometry. Select stability-related properties of the two B100's and two B20's were also measured after JFTOT stressing. All data was evaluated and correlated to provide further information on how stability-related properties impact a biodiesel fuel's deposit-forming tendency, and how hot steel-surface stressing can further affect stability.

SESSION 4: BIOFUELS II: BIODIESEL STABILITY

KEYNOTE: A BROAD OVERVIEW OF THE STATUS OF BIODIESEL IN THE US

Robert L. McCormick

Biodiesel is a fuel blending component produced from fats, vegetable oils, and waste cooking oils by transesterification to form fatty acid esters. These are typically fatty acid methyl esters of FAME if methanol is used as the reactant alcohol. Biodiesel production in the United States has grown approximately ten-fold since the introduction of a blender's tax credit for in January 2005, perhaps reaching 300 million gallons in 2006. The tax credit provides \$1/gal for agri-biodiesel (animal fat or vegetable oil-based) and \$0.5/gal for biodiesel from waste oils. However, a number of unresolved technical issues are limiting growth. These include: 1) Lack of quality specifications (ASTM standards) for biodiesel blends. Blend specifications have not yet passed ASTM because of poor understanding of how biodiesel affects blend stability and low temperature performance, among other issues; 2) Poor understanding of how biodiesel blends impact engine durability, operational costs, and maintenance practices. A key issue being the effects of biodiesel on water separator performance; 3) A need for more representative data on the effects of biodiesel blends on pollutant emissions; 4) Little data on the performance of advanced emission control technologies such as diesel particle filters and NO_x reduction catalysts, including impact on filter/catalyst durability. This presentation will provide an update on the status of each of these issues, including new data, and more in-depth description of U.S. biodiesel markets.

CHEMISTRY OF BIODIESEL INSTABILITY

Jack Burgazli

Bio Diesel is the fastest growing liquid fuel on the market. As with introduction of any new product, certain issues and concerns must be addressed. The paper discusses information relating to the chemical pathways of bio diesel degradation, and the environmental and chemical factors which affect bio diesel stability.

OXIDATION AND STORAGE STABILITY OF BIODIESEL AND BIODIESEL BLENDS

Robert L. McCormick & Steven R. Westbrook

This paper presents the results of work conducted to develop a database that supports specific proposals for a stability test and a specification for biodiesel and biodiesel blends. The overall study included the following steps: 1) Collection of 19 B100 samples and six diesel samples; 2)

Preliminary B100 characterization and measurement of B100 stability using accelerated tests; 3) Down selection from 19 B100 samples to eight that cover the range of stability observed in accelerated tests and the range of feedstocks; 4) Preparation of B5 and B20 blends from eight biodiesel fuels and six diesel fuels; 5) Measurement of the stability of the B5 and B20 blends using accelerated tests; 6) Down selection from 48 B5 and 48 B20 blends to eight of each blend; 7) Testing of the eight B100 samples for stability in a simulated storage environment for 12 weeks; 8) Testing of the eight B5 and eight B20 blends for stability in a simulated storage environment for 12 weeks, and in a simulated vehicle fuel tank for 1 week followed by high-temperature stability testing; 9) Selection of two B100 and two diesel fuels for tests of antioxidant additives in all testing scenarios. The results of the testing of the down selected fuels, the B5 blends, and the B20 blends are presented and discussed.

OXIDATIVE STABILITY OF BIODIESEL—METHODS, TOOLS, AND TECHNIQUES FOR ASSESSING THE EXTENT OF DEGRADATION

Sharon M. Cline and Thomas E. Carter

Biodiesel is a renewable fuel manufactured from vegetable and animal oils. As such, it is susceptible to the same oxidative processes that cause rancidity in these materials. The byproducts of these processes in biodiesel are high molecular weight oligomers, and/or oxidized break-down products, often aldehydes or organic acids. These unwanted byproducts pose potential problems in internal combustion engines due to insolubility and/or corrosivity. The Oil Stability Index, OSI, provides a measure of the oxidative stability of biodiesel. Other analytical techniques and determinations, such as UV absorbance, peroxide value, Gel Permeation Chromatography (GPC), and GC-MS, provide additional insight to the oxidative process. Data from these various techniques have been used to follow the oxidative aging in biodiesel. The effectiveness of oxidative stabilization of biodiesel with several antioxidant formulations, and the impact of possible biodiesel handling issues such as air intrusion and storage temperature is presented.

EVALUATION OF ANTIOXIDANTS ON STABILITY-RELATED PROPERTIES OF BIODIESEL: EFFECT OF ANTIOXIDANT CHEMICAL STRUCTURE ON ANTIOXIDANT PERFORMANCE

J. Andrew Waynick, William E. Moehle, Vince Gato, and Steven R. Westbrook

The effect of nine antioxidants of known chemical structure was evaluated in a soy-based, additive-free B100 that had poor stability but was otherwise ASTM D6751 compliant. The nine antioxidants evaluated included four non-functionalized phenolics, three functionalized phenolics, and two amine-based antioxidants. Each of these additives was added to the B100 at both 1,000 ppm and 2,000 ppm. The additive-free B100 and the 18 additized B100 samples were evaluated according to five stability-related tests: Rancimat (EN 14112), modified D2274 total insolubles, modified D2274 iso-octane insolubles, Post-D2274 Total Acid Number (TAN), and Post-D2274 Peroxide Value (PV). Results of the additized fuels were compared against the additive-free B100, both before and after D2274 stressing, as appropriate. These five test variables were also cross-correlated to reveal more information concerning the performance of

the nine antioxidants. Results indicated that the best overall antioxidants were two non-functionalized phenolics, MBDTBP [4,4'-methylenebis(2,6-di-tert-butylphenol)] and BHT (butylated hydroxytoluene). Another phenolic, DTBP (2,6 di-tert-butylphenol) as well as one functionalized phenolic, DTBDMAC (2,6-Di-tert-butyl-alpha-dimethylamino-p-cresol, which is a tertiary amine modified phenolic) and one amine-based antioxidant, PDA (phenylene diamine) also gave good performance. The amine-based nonylated diphenylamine (NDPA) was completely ineffective in inhibiting D2274 total and iso-octane insolubles or in reducing Post-D2274 TAN and PV. All additives that gave low D2274 total insolubles also gave low iso-octane insolubles. Additives that gave the best performance in the D2274 test also gave the lowest Post-D2274 TAN values. Rancimat induction period (IP) did not in general correlate well with any other variable. However, all additives that imparted very high Rancimat IP also gave excellent modified D2274 results.

IMPROVEMENT IN STORAGE STABILITY OF BIODIESEL WITH SYNTHETIC ANTIOXIDANTS

Dr. Axel Ingendoh

Biodiesel without antioxidants is unstable and quickly becomes rancid. Rancidity is a type of oxidation by air in which short-chain fatty acids and insoluble polymers are formed. Both side products can cause engine damage by corrosion or through the formation of deposits. It has been shown that the content of natural antioxidant Vitamin E in rape seed oil biodiesel is mostly insufficient to ensure that the level specified in the EU standard of 6 h in the rancimat test at the filling station can be maintained. Test results are presented which show the correlation of rancimat value, Vitamin E concentration and shelf life of biodiesel. The new Baynox® synthetic antioxidants for rape seed biodiesel, palm biodiesel and animal fats show a dramatic increase in rancimat values and increase in shelf life accordingly. Biodiesel produced from soybean oil shows less effects on Baynox® as expected. The course was investigated and attributed to the higher content of multiple unsaturated fatty acid methylester in soybean biodiesel. This was proved by testing rancimat values on pure Palmitic-, oleic-, linolic- and linoleicmethylesters. Screening of highly active antioxidants led to the development of Baynox® plus, a second biodiesel antioxidant with strong activity in soybean and sunflower biodiesel. Test results in soybean biodiesel from the market and vitamin E free biodiesel produced by distillation are shown and prove the superior activity of Baynox® plus. In the presentation the mechanism of oxidation and the mode of action of antioxidants is discussed. Additionally, some examples are presented which show, where the yellow color of biodiesel really comes from and how one can actually visualize the oxidation leading to rancidity and gum formation.

SESSION 5: FUEL FILTRATION & CLEANLINESS

THE USE OF ELECTRONIC SENSORS IN FIELD MEASUREMENTS OF AVIATION JET FUEL CLEANLINESS

Anthony Kitson-Smith, and Vic Hughes

For decades, conventional technologies and procedures have been used in the cleanliness control and monitoring of jet fuel delivered to aircraft. In recent years the aviation fuelling industry has realised that “fail-safe” as a concept applied to fuel cleanliness, requires not only continuous improvement but also development and deployment of a range of technologies to maintain relevance. Continuous improvement of existing filtration technologies is encouraged in new editions of existing standards but step change is difficult to realise when they are already highly developed. Use of non-traditional technology to augment current practise is needed. An earlier paper reviewed the most promising technologies available at that time and described initial laboratory experience with them. Since then a new industry standard (API/IP 1598) has been published detailing requirements for electronic sensors and draft laboratory test methods published. This paper will briefly summarise and update this position and describe early field experience gained by trialling a number of the most promising fuelling vehicle sensor technologies. Fuel cleanliness control and monitoring looks set to meet the challenges of an expanding 21st Century Aviation fuel business.

EVALUATION OF OLD AND NEW TECHNIQUES FOR MEASURING CLEANLINESS OF DISTILLATE AND BIOFUELS

Rick Chapman, Mike Sherratt and Jim Crighton

Fuel cleanliness testing requirements are becoming more stringent due to the design of modern engines and fuel systems, longer service intervals plus concerns about microbiological growth and the low temperature performance and storage stability of biodiesels. Appearance and gravimetric tests have been used successfully for over 100 years but are essentially manual methods that rely on operator judgement and technique. This can result in poor precision and results that are often not as reliable as expected. New or improved automatic techniques can offer more precise and faster results with less operator effort. However, since measurement principles for these new techniques are fundamentally different from existing techniques, there will be issues regarding equivalence criteria that will have to be addressed before these new methods could be considered for use in fuel specifications. This paper discusses the development of new and improved techniques and compares their performance, precision and results for a wide range of distillate and biofuels.

THE NEXT GENERATION FREE WATER SENSING TECHNOLOGY

Steven D. Anderson and Alex Marshall

The International Air Transport Association (IATA) Guidance Material for Aviation Turbine Fuel Specifications specifies that the concentration of undissolved or ‘free’ water in aviation kerosene shall not exceed 30ppm at point of delivery to the aircraft. The Air Transport

Association (ATA) of America Specification 103 requires that the free water concentration downstream of receiving and dispensing filtration shall not exceed 15ppm. Free water constitutes not only slugs of water but also emulsified water droplets which are suspended in the fuel. Free water is a fuel contaminant and limits have been established to prevent the formation of ice crystals which can block fuel flow to the engine and can support microbiological contamination, contributing to the corrosion of metallic components. Testing of aviation kerosene at the point of delivery to the aircraft is crucial to verify that the level of free water is below the specification limits and that water removal systems are operating satisfactorily. A number of test kits are available for this purpose which operate under the general principle of contacting a fuel sample with a water sensitive medium which indicates the presence of free water by changing color. In this paper we discuss the relative merits of these tests as well as disclosing the latest developments of the next generation free water sensing technology.

MEDIA MIGRATION FROM AVIATION FUEL FILTER MONITORS

Paul P. Wells

This paper describes the development of a laboratory-scale test rig to assess media migration from filter monitors and summarizes results of a study to quantify media migration from 2” aviation fuel filter monitors. Filter monitors from three different manufacturers are evaluated at both a high and low fuel flowrate, with and without the addition of water contamination. Filter monitors, which capture both dirt and water contamination, have been used for many years in aviation fuel distribution systems. Recently, the military reported several in-flight jet engine failures on the same day at the same base. These failures were reported to be caused by the blockage of on-board fuel filters with super absorbent polymer (SAP) originating from filter monitors. The tests reported herein explore the propensity of filter monitors to release SAP into jet fuel representative of that used in the commercial sector, containing no DiEGME icing inhibitor. (Unlike the military, jet fuel used in commercial aviation does not usually contain DiEGME.)

DETERMINATION OF THE EFFECTS OF FUEL SYSTEM ICING INHIBITOR (FSII) CONTAINING DI-EGME ON IP 1583 4TH EDITION WATER ABSORBENT MONITORS

Gary B. Bessee and Jeremy Tucker

The objective of this program was to determine the filtration effects using di-EGME in F-34 aviation fuel. Tests were performed using with the 50-ppm water and water slug sections of API/IP 1583 4th Edition. The test stand was configured to operate in a single pass mode. API/IP 1583 4th Edition 2” water absorbent monitors were evaluated to determine the water holding capacities using F-34 fuel with and without fuel system icing inhibitor (FSII). Di-EGME was used as the fuel system icing inhibitor for all of the evaluations. The water injection flow rates were used based on the monitors operating at rated flow: 20, 40, 50, and 100 ppm. Water challenges ranging from 20 ppm to 100 ppm were used with both test fuels to determine any differences when the monitors were exposed to FSII (Di-EGME). All the analytical methods (free water by Aqua-glo, turbidity, and particle counting) agreed that the fuel containing FSII has

detrimental attributes to water removal efficiency. Similar results were found when performing the water slug tests. This work augments earlier results produced by DCSEA under contract to the Energy Institute (2000) in which testing with a 3rd Edition 1583 Velcon 2" water absorbent monitor demonstrated unacceptable performance in F-34 containing di-EGME.

USED AIRCRAFT FILTER ANALYSIS – DETERMINING SAP PRESENCE/ABSENCE

Krystal B. Wrigley

The Aviation Industry has expressed concern over shortened aircraft filter life. They are interested in determining 1) the composition of the material plugging the filter and 2) if SAP (Super Absorbent Polymer) has migrated from the filter monitor and contributed to the debris causing filter plugging. Work was recently undertaken to assess the materials present on commercial aircraft filters and what role, if any, SAP has in the plugging (media migration). This paper describes the techniques used to determine presence/absence of SAP on aircraft filters through laboratory and analytical methods. A detailed compositional analysis of discrete particles in the filter debris was also investigated.

SESSION 6: ANALYTICAL METHODOLOGY

A PORTABLE SOFTWARE IMPLEMENTATION OF CHEMOMETRIC MODELING FOR RAPID FUEL QUALITY ASSESSMENT

Robert E. Morris, Kevin J. Johnson, Mark H. Hammond, Kirsten E. Kramer, Jeffrey A. Cramer and Susan L. Rose-Pehrsson

The Naval Research Laboratory has been engaged in a Navy Fuels & Lubes IPT initiative to develop rapid automated shipboard fuel quality surveillance technologies. This approach is based upon deriving mathematical relationships between analytical fuel data and measured specification properties. In the first phase of this study, we successfully demonstrated the use of chemometric-based modeling to predict a range of fuel properties from analytical data (Johnson, et.al., Proceedings of the 9th IASH Conference, p. 482-500). We are currently developing a portable stand-alone software implementation of this fuel property modeling that will rapidly estimate a range of specification fuel properties of jet and Naval distillate fuels, from a single analysis by capillary gas chromatography, near-infrared spectroscopy and Raman spectroscopy. This application will form the basis for the control, acquisition and data analysis components of fuel quality assessment instrumentation for shipboard and land-based use. A further implementation of this technology will be for in-line sensors to provide real-time fuel grade and specification property monitoring. Each incoming fuel is classified as jet (JP-5, JP-8, Jet A) or diesel (F-76), and the relevant properties for each type are calculated and reported. As our training set is more fully developed, we expect the prediction accuracy to improve accordingly. Calibration transfer is a major challenge in developing a modeling application that is suitable for widespread use with different instruments. This presentation will summarize the current capabilities and limitations of the fuel property prediction algorithms, in addition to identifying current computational issues we are working to resolve.

THE DEVELOPMENT OF AUTOMATED ANALYTICAL METHODS TO PREDICT FUEL PROPERTIES BY UNATTENDED SOFTWARE

Jeffrey A. Cramer, Kirsten E. Kramer, Kevin J. Johnson, Mark H. Hammond, Susan L. Rose-Pehrsson and Robert E. Morris

The Naval Research Laboratory, as part of the Navy Fuels & Lubes IPT rapid fuel quality surveillance initiative, is currently developing a stand-alone software package that can provide an accurate prediction of jet and diesel fuel specification properties using only in situ sensor data. Sensor data from near-infrared spectroscopy, Raman spectroscopy, and capillary gas chromatography are being used in this work. In order for this package to perform adequately regardless of operator expertise, automated data assessment and pretreatment tools need to be developed based on the requirements of the analysis itself. Automated tools such as these have critical prerequisites such as a universal or immediately quantifiable applicability, so that they can be used on either all of the sensor data or only certain facets of the data, at the software's own unattended discretion. It is also vital that the predicted specification properties be presented with a realistic measure of the associated uncertainty that would allow operators of all relevant skill levels to assess the reliability of the results. This involves the development of novel methodologies to propagate not only the modeling errors, but also data quality and the uncertainties inherent in the reference ASTM measurements that are used to develop the predictive models. Specific problems, such as the aforementioned error quantification, model creation and maintenance, and data preprocessing, have already been addressed. This presentation will discuss some of the analysis challenges encountered so far in the creation of the software package as well as the novel solutions that have been applied to overcome said challenges, focusing on the mathematical and statistical methodology.

STUDIES OF THE KINETICS OF JET FUEL THERMAL STABILITY BY LASER INDUCED FLUORESCENCE

Dr. Clifford A. Moses and George R. Wilson III

Thermal stability is a characteristic that relates to a fuel's ability to resist the formation of deposits when passed over a heated surface. This is an important fuel property because the fuel is used to cool the engine oil as well as electronics, and any deposit would reduce heat transfer efficiency. Additionally, the fuel must pass through the fuel nozzle without leaving deposits that would increase the pressure drop or partially block the exit orifice; such deposits could then lead to hot streaks, non-uniform temperature profiles, and/or ignition difficulties. Thermal stability is becoming a greater issue with modern military and civilian aircraft engines as the cycle temperatures increase to achieve greater efficiency. Thermal stability is not measured as a fuel property; it is evaluated secondarily as the color, weight, or thickness of deposit left on a heated tube in a deposition test. This deposit is not a property of the fuel. It is an artifact of the deposition test, i.e., the flow rate, temperature, and thermal history of the fuel. The authors contend that thermal stability, as a fuel property, is the formation rate of the precursors to these deposits. It is the variables of the flow system that then determine the deposition rate. This paper summarizes the results of experiments using laser-induced fluorescence to study the kinetics of the formation of deposit precursors.

A NEW REALISTIC LABORATORY SCALE FUEL OIL FILTRATION TEST

Wil J.M. Stassen, Koen Steernberg, Jacco D.M. Woldendorp, Arjen Nieuwhof, Frans G.A. van den Berg, and Klaus Schlame

Heavy fuel oil may contain small amounts of sediments. These originate either from crude oil itself (silt and clay), from the refining process (e.g. catalyst fines) or are formed or picked up during transportation and storage (sludge, rust particles, other contaminants). Installations using heavy fuel oil are normally designed to deal with small amounts of such sediments. However, from time to time fuels appear in the market, which cause serious filtration problems, in extreme cases even causing failure of the equipment. In many cases these problem fuels met all the standard specifications for total sediments. In order to evaluate various filtration problems in a performance related fashion, Shell Global Solutions has designed and built a novel filtration test rig, capable of simulating for the time the filtration process under application-oriented or field conditions of temperature, pressure and, most importantly, linear liquid velocity. The new unit consists of a heated storage vessel, a filter housing containing a 47 mm round piece of commercial filter material, an integrated electronically controlled flow meter + pump and a sensitive pressure difference indicator measuring the pressure drop over the filter as a function of time. The test rig can be used to simulate actual problem conditions, but in the course of this work we have also developed a standard test for comparing different fuels. The standard test, which has been validated using a range of normal and problem fuels, uses a 10 micron stainless steel filter from Boll & Kirch. Fresh fuel is heated to obtain a viscosity of 35 cSt and pumped over the filter at a linear liquid velocity of 1 kg/cm² filter surface area/hour for a period of four hours. The pressure drop over the filter is recorded as a function of time and converted into a Filterability Index (FI). After each test, the filter with adherent deposits can be easily removed for further investigations by independent analytical techniques such as elemental analysis, scanning electron microscopy (SEM), infrared (IR), etc. During the presentation the use of the test rig will be explained and illustrated with several practical examples.

MEASUREMENT OF LIQUID PHASE H₂S IN RESIDUAL AND CRUDE OILS

Mike Sherratt and Andy Woodward, Jim Crighton and Wanda Fabriek

Hydrogen Sulfide (H₂S) is a very toxic gas and at certain concentration levels can be fatal. It is a natural component in crude oils and an unwanted by-product of residual fuel manufacture. Over many years the presence of H₂S has been identified globally within refineries, terminals and fuel oil storage systems, during bunkering or fuel handling on board ships as well as during carriage and handling of crude oil. Vapour phase measurements are relatively simple to carry out but are strongly influenced by the amount of H₂S in the liquid phase, temperature, headspace and the degree of agitation. Measurement of H₂S in a liquid phase is much more difficult. Liquid phase measurements provide an indication of the amount of H₂S that can potentially be generated in the vapour phase. The liquid-phase measurements are therefore the best approach for measuring safe levels of H₂S. The Energy Institute's laboratory spectrophotometric test method IP 399 can be considered the industry norm for providing liquid phase results, but the procedure can take 3 hours. This paper includes the development of a new lab-portable instrument to determine the content of H₂S in liquid samples of crude oils and fuel oil. This development has involved a number of crude and marine fuels, with measurement times less than 20 minutes, with a limit of

detection at sub ppm levels. The apparatus is automated and does not require significant analytical expertise. The presentation will review the technology applied, test / correlation results and the implementation of the new lab-portable instrument for this new exciting technology development that was developed in collaboration with Lloyds Register EMEA Group and the international oil industry.

SESSION 7: ADDITIVES & ADDITIVE RELATED PROPERTIES

THE NEED FOR STATIC DISSIPATOR ADDITIVES IN ULTRA-LOW SULFUR FUELS AND RECENT DEVELOPMENTS

Cyrus P. Henry Jr.

This paper reviews electrostatic principals relevant to ultra-low sulfur diesel fuels. It also reviews recent developments, including efforts to further define the effects of sulfur oxides on the conductivity of jet fuels.

ULSD – IMPACT ON FUEL CONDUCTIVITY

Jack Burgazli

Desulphurization of diesel fuels to meet EPA emission requirements has greatly affected diesel fuel properties. The paper discusses desulphurization impact on fuel conductivity, the performance of Static Dissipater Additives in ULSD and the interaction of Static Dissipater Additives with Lubricity additives.

SOLUBILITY CONCERNS WITH ADDITIVES

Paul M. Ryder

For years, industry has seen instances of fuel filter plugging with a black organic material that could not conclusively be identified. Extensive analytical work has led to the conclusion that a certain chemistry of additive may have a tendency to precipitate out of clean fuels- gasoline and diesel fuel in particular. The black mystery substance has been identified throughout the distribution system- fuel terminals (tank bottoms/filters), retail outlets (filters), and ultimately customers' vehicles (filters/injectors). Analytical methods used to investigate and characterize the matter included FTIR (Fourier Transform InfraRed), DPMS (Direct Probe Mass Spectrometry), LCMS (Liquid Chromatography Mass Spectrometry), and NMR (Nuclear Magnetic Resonance). Components much higher in molecular weight than the active ingredients of the fuel additives in use were found in some samples of both the additives and the bottoms of fuel storage tanks. In the filter sludge, there appeared to be a high concentration of the high molecular weight components. Thus, it was concluded that high molecular weight components in the additive precipitated out of the fuel. Despite these discoveries, there are still some concerns regarding this chemistry of additive. In particular, there is no simple quality assurance method to ensure the additives will not have the high molecular weight components in them.

ConocoPhillips will continue efforts to ensure the problem is permanently resolved, including developing a test method to measure the heavy material.

INVESTIGATION INTO THE RAPID DEGRADATION OF US NAVY SHIPBOARD DIESEL FUEL

Sherry A. Williams, Richard A. Kamin, Robert W. Fowler, Carole L. Jessee, Henry H. Zion

Beginning mid-2004, the Naval Fuels team began receiving numerous phone calls and messages regarding excessive filter change-outs onboard Naval vessels. The problem was isolated to ships that had recently received fuel from east coast naval fuel depots or oilers. During the same timeframe, the Coast Guard experienced gas turbine failures onboard two ships. The Navy spent approximately \$1.2 M on additional filters during this fuel quality problem and the Coast Guard spent approximately \$1.9 M to repair their damaged engines. Laboratory reports showed that the fuel was on specification at procurement. Fuel samples pulled from the affected depots showed that the fuel remained on specification at the storage depots. However, field samples obtained from various ships showed a very dark, almost black fuel. Particulates exceeded the Navy's limit of 10 mg/L in almost all cases, even those pulled after the filter coalescers. Samples of coalescer elements showed a black, tarry material had penetrated both the inlet and outlet sides of the filters. The origin of the fuel was traced back to one refiner. A Navy approved fuel stability additive was being added to the fuel. The root cause of the problem was determined to be a combination of poor laboratory procedures at the refinery lab and ineffectiveness of the stability additive being used. The Navy has since removed the allowance for using the stability additive from the military specification for F-76 shipboard diesel fuel. This paper discusses the investigation into rapid diesel fuel degradation experienced by the US Navy and Coast Guard in the 2004/2005 timeframe.

LOSS OF FUEL SYSTEM ICING INHIBITOR ADDITIVE DURING FUEL TRANSPORT AND STORAGE

Steven K. Shaeffer

This paper is a description of an effort by the US Air Force to estimate the extent to which Fuel System Icing Inhibitor (FSII) additive is lost from JP-8 during the routine transport and storage of this fuel. This is a work in progress and is a subset of a larger Air Force study to determine if the current minimum FSII concentration requirement for JP-8 can be lowered without affecting the capability to inhibit the freezing of any existent free water. Loss estimates are derived from the FSII concentration data taken from 40 different Air Force bases located in a variety of geographic regions over a twelve month period of time. For each base, FSII concentration values have been collected from multiple points in the fuel logistic train stretching from the source to the point of issue. FSII loss at a particular base is evaluated in terms of the differences in the mean concentrations observed at that base. Since the loss of FSII is anticipated to be largely due to its extraction from the fuel by free water, correlations between additive loss and delivery mode, location, and local seasonal weather conditions are examined for any cause-and-effect inferences.

DETERMINATION OF MINIMUM REQUIRED FSII DOSAGE FOR USE ON USAF AIRCRAFT

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

Fuel System Icing Inhibitor (FSII) is one of the three required additives in U.S. military aviation fuels JP-5 and JP-8. The primary function of the FSII is to prevent solidification of aqueous liquid within the fuel, which could adversely affect fuel system operation. Di-Ethylene Glycol Monomethyl Ether (DiEGME) is the currently approved FSII, with a required procurement dosage of 0.10-0.15% by volume for both fuels. The use limits are currently 0.03% (JP-5) and 0.07% (JP-8), respectively. Many motivating factors, ranging from logistical/economic issues to application-based concerns, exist for determining if the required procurement and use limits can be reduced. Lower FSII requirements could significantly reduce associated logistical footprint and procurement issues and would render a considerable cost savings. In addition, environmental and material compatibility concerns related to DiEGME could be significantly alleviated. Due to the varying system complexity and flight regimes experienced by different aircraft platforms, it is difficult to evaluate the required DiEGME dosage for all applications independently. It is beneficial to improve the understanding of the manner by which the FSII prevents ice formation, how it interacts with free and dissolved water, and how it functions in a flowing system. Therefore, studies were undertaken to provide an improved understanding of how FSII functions, especially related to pertinent operating variables. Specific efforts included estimation of the anticipated total water content within aircraft fuel systems, partitioning of FSII between fuel and aqueous phases at sub-ambient temperatures, and flow testing to investigate blockage due to icing. The goal of the overall program is to provide a quantitative basis for the minimum required FSII dosage while maintaining safe operability. An overview of the individual efforts will be provided and experimental data and implications will be discussed.

DEVELOPMENT OF ALTERNATIVE FUEL SYSTEM ICING INHIBITOR ADDITIVES THAT ARE COMPATIBLE WITH AIRCRAFT TANK TOPCOAT MATERIAL

Steven Zabarnick, Zachary West, Matthew J. DeWitt, Linda Shafer, Richard Striebich, and Charles L. Delaney, and Donald Phelps

In recent years there has been an increasing incidence of reports of the peeling of topcoat material in the ullage space of integral wing tanks in the B52 and other military aircraft. This increase in delamination phenomena coincides with the change from JP-4 to JP-8 as the primary U.S. Air Force fuel and also the change in primary icing inhibitor additive from ethylene glycol monomethyl ether (EGME) to diethylene glycol monomethyl ether (DiEGME). Recent work indicates that with the JP-8/DiEGME combination, the icing inhibitor additive can concentrate in the tank ullage and condense at these high concentrations on the upper tank walls. These high concentrations of DiEGME cause swelling and subsequent peeling of the epoxy-based topcoat. In this work we report on the identification and evaluation of alternative icing inhibitor additives that do not cause topcoat delamination in fuel tank upper surfaces. Initially, prospective additives need to be evaluated for their ability to inhibit the formation of ice in aircraft fuel systems. Additives which perform well as icing inhibitors then need to be evaluated

for their compatibility with fuel tank topcoat material. The initial group of additive candidates evaluated consisted of glycol ether species with decreased volatility. These low volatility species should be less able to concentrate in the ullage and cause topcoat failure. Subsequent testing will involve compatibility with other fuel system materials, evaluation of the effect on fuel properties such as thermal stability, impact on fuel filtration, impact on functionality of other additives, and testing of the biostat capabilities of the additive.

UPDATE ON THE ENVIRONMENTAL FATE AND ECOTOXICOLOGY OF THE ISOTHIAZOLONE BIOCIDES

Howard L. Chesneau, Edward W. English, II

The environmental characteristics of industrial biocides are of great concern and constantly being evaluated due to increasing regulatory pressure to be current on environmental exposure, handling and disposal issues. All this information is provided in the Material Safety Data Sheets (MSDS) supplied to and available to the customer. Since the initial report in 2003 there have been some changes to the hazard summary, hazard class in the shipping and handling section and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) information with regards to Isothiazolone biocides. Isothiazolone biocides are broad spectrum antimicrobials used in a variety of industrial applications. This presentation will focus on changes made to the hazard summary, shipping and handling hazard class and the CERCLA information in the MSDS. Biocides are employed to control or eradicate microbial growth in numerous applications. The ideal biocide shows good efficacy in a broad spectrum of activities and should be stable in the formulated end product. In addition the ideal biocide should have the following environmental characteristics: 1) Rapid degradation in the environment; 2) Rapid partitioning in the environment resulting in limited bioavailability to non-target organisms; 3) Minimal toxicity to non-target organisms at concentrations present in the environment; 4) Minimal bioaccumulation of toxicologically significant compounds. With the ever changing regulations biocide assessments for the above characteristics must be performed to ensure compliance and confirm original data. These studies determine the risk assessment as a function of both the exposure and the hazard. The exposure, which is a measure of the concentration of the biocide in the environment, is affected primarily by degradation and partitioning. The hazard represents the toxicity of the biocide to non-target organisms. Low risk is obtained when the environmental concentration of the biocide (exposure) is less than the toxic threshold. These characteristics determine the hazard class, hazard summary, shipping and handling procedures and disposal requirements. This information is compiled in the MSDS and provided to the customers. Isothiazolone biocides are effective at low concentrations, therefore provides low employee and environmental exposure when used and disposed of as directed in the MSDS.

SESSION 8: MICROBIOLOGICAL CONTAMINATION OF FUEL

MICROBIAL CONTAMINATION STUDIES IN JP-8 FUELED AIRCRAFT

Marlin Vangsness, Capt. Sarah Chelgren, Ellen Strobel, Lori Balster, Loryn Bowen, and Susan Mueller

In 2003 the fuels laboratory at Wright Patterson AFB initiated a study to investigate the level diversity of microbes in Air Force fuel systems. Samples were taken along fuel distribution paths starting at several refineries and included pipeline samples, barge samples, truck tanker samples, base storage samples, and several aircraft to construct a representative contamination profile. Instead of finding a primary contamination site, bacteria and some fungi were found throughout the distribution system. In 2005 the program emphasis was changed to focus on contamination in aircraft fuel tanks. Samples were taken from civilian aircraft in long term storage as well as from Air Force line aircraft. Cargo and bomber aircraft were sampled across the continental US. Water bottoms were noted and DiEGME concentration was measured as well as ATP levels and Colony Forming Units. Microbes were cultured for identification using PCR and DNA sequencing. While many species historically associated with fuel contamination have been found, several species not previously reported have also been identified. In recent years there has been mounting pressure to reduce fuel costs in the Air Force. DiEGME, the current FSII additive, is added to JP-8 at a maximum volume percentage of 0.18 and is an obvious candidate for cost reduction. In addition to its function as an anti-icing additive it also performs as an anti-microbial at high concentrations in water bottoms. This recent study has documented that measurable amounts of water can be found on many aircraft where fuel sumps are not drained with regularity. During the 2005-2007 period, one liter aircraft sump samples ranged from dry fuel only to samples with more than 200 ml of water / DiEGME. DiEGME concentration in water bottoms was typically more than 30%, (In fact it ranged from 32% to 50%.) While microbes were found in fuel without a measurable water phase, no evidence of microbial activity was found in water containing high concentrations of DiEGME. Measurements of ATP, (adenosine triphosphate), for the most part indicated minimal microbial activity while several tanks gave ATP readings normally associated with significant microbial populations. Since none of the line aircraft reported any evidence of noticeable contamination, it is still not evident what level of ATP is cause for concern.

INVESTIGATION OF GENE ACTIVATION OF BACTERIAL SPECIES ISOLATED FROM UNITED STATES AIR FORCE AVIATION FUEL USING DNA MICROARRAYS

Michelle E. Rauch, Brandon R. Martinez, Jonathan S. Stralka and Katherine Todorov

Since the United States Air Force (USAF) assumed use of a kerosene-based aviation fuel it has been well documented that that the fuel can be degraded by microorganisms. However, the ability of the bacteria and fungi to sequester the fuel and suspend it within the aqueous phase for subsequent metabolism, particularly in aviation fuel, is not well understood. The microorganisms present with the water bottoms of fuel storage tanks have been shown anecdotally to produce surfactant and or polymer molecules as evidenced by the disarming of refuelling truck filter/coalecers. As described in Rauch et al (2006) a 2002-2003 Air Force Research Laboratory

(AFRL) study isolated ten genera of bacteria from USAF aviation fuel storage tanks. Of those ten genera the organism *Bacillus licheniformis* was found to be the most prevalent at the eleven USAF bases sampled. *Bacillus licheniformis* has been shown to produce a high molecular weight poly-glutamate polymer. There is some evidence that a negatively charged carboxyl containing polymer may indeed bind to and reduce the corrosion of a metal surface. While isolation of individual suspected polymer species produced by *Bacillus licheniformis*, *Dietzia* sp. and other microorganisms is feasible, advances in identifying and quantitating mRNA transcripts opens an avenue to expeditiously investigate organism expression of multiple proteins/polymers. Exploitation of DNA microarrays allows researchers to visualize which genes are being expressed in a particular organism or cells. Knowing which genes are expressed by probing for complementary mRNA gives information as to what proteins are being ordered into production upon cell exposure to a particular environment, without the actual production or isolation of those proteins. This paper describes the use of DNA microarrays to exam which genes are “turned on” upon *Bacillus licheniformis* exposure to JP-8. The data provides crucial insight as to how the bacteria metabolizes the aviation fuel resulting in protein/polymer products. The application of this information may in turn unveil potential chemical indicators of aviation fuel microbial contamination which may be exploited for detector design or other novel uses.

MOLECULAR SYSTEMATICS AND GENETIC FINGERPRINTING OF HYDROCARBON-DEGRADING BACTERIA IN FUEL SAMPLES

Judith White, Andrew J. Weightman, Graham C. Hill, Edward C. Hill and Eshwar Mahenthiralingam

Microbial spoilage of hydrocarbon fuels is a widespread problem for the oil industry. The inability to grow contaminants and complex taxonomy of many bacterial species often limits the effective identification of the spoilage organisms by routine microbial culture. Molecular techniques provide a rapid and effective means to overcome the latter problems. We developed a strategy to examine the bacteria associated with fuel spoilage that combined cultivation with: (a) genetic fingerprinting to identify strains associated with contamination, and (b) 16S rRNA gene sequence analysis to facilitate their systematic identification. A total of 30 samples of contaminated fuels from a range of sources were analysed. PCR fingerprinting of single colonies was performed by Random Amplified Polymorphic DNA (RAPD) analysis enabling a collection of genetically unique contaminating strains to be assembled. This avoided unnecessary repetitive analysis of the same strain within a given sample and from an industrial perspective, the genetic fingerprinting also formed a means to track single strains and to identify the source of contamination. 16S rRNA gene sequencing of 65 cultivable strains identified the following distribution of contaminating bacteria: 83% were Gram negative including 15 *Pseudomonas* sp., 1 *Serratia* sp., 3 *Marinobacter* sp., 8 *Burkholderia cepacia* complex sp., 1 *Shewanella* sp. and 1 *Pantoea* sp, and 17% were Gram positive including *Bacillus* sp., and *Staphylococcus* sp. In summary, a combined approach of cultivation and molecular analysis of bacterial fuel contamination revealed a diversity of causative species. The techniques show possibilities for tracing problematic sources of contamination and for development of rapid identification tests and novel strategies to prevent biofouling.

USING ADENOSINE TRIPHOSPHATE CONCENTRATION AS A MEASURE OF FUEL TREATMENT MICROBICIDE PERFORMANCE

Frederick J. Passman, Edward English, and Charlotte Lindhardt

Although Adenosine Triphosphate (ATP) has been used to estimate microbial biomass in aqueous systems for more than fifty years, it has only been adopted for use with fuels and fuel-associated water during the past several years (Passman et al. Non-conventional Methods for Estimating Fuel System Bioburdens Rapidly. In: R. E. Morris. Ed. Proceedings of the 8th International Conference on the Stability and Handling of Liquid Fuels; 14-19 September 2003, Steamboat Springs, CO.) This paper reports the evaluation of ATP as a parameter for evaluating the performance of fuel treatment microbicides. Additionally, it presents ATP test repeatability data developed as part of the ASTM test method development process. Test results from two ATP test protocols are compared. Additionally, ATP data are compared with culture data on the basis of speed of data availability and test precision.

ATP ANALYSES AS A TOOL TO DETERMINE THE NEED TO CLEAN THE FUEL TANKS OF DIESEL MOTIVATED VEHICLES BEFORE REFUELING WITH BIOCIDES AND STABILITY IMPROVING ADDITIVES

J. Geval, E. Geissmann, E. Ittah, I. Nakdimon, Y. Sapir and R. Fass

Stabilizing additives and biocides may enhance the suspension of organic and microbial sediments that accumulate in Diesel fuel tanks of vehicles during long term storage. This could lead to fuel filters blocking immediately upon the release of the vehicles from storage. We have investigated the possibility to use the Microbial Contamination Level (MCL) and ATP contents of clear diesel fuel samples withdrawn from vehicles, between storage intervals, as criteria for judging the need to clean the vehicle's fuel systems before the addition of such additives. Bottom fuel samples taken from fuel cells of combat vehicles in storage, were analyzed for their MCL using the traditional live counts laboratory method. The source fuel tanks were dismantled from the vehicles, opened and inspected for significant visual internal contamination. MCLs higher than 5000 molds/liter fuel were found to correlate to a high contamination level that justifies an intensive cleaning of the vehicle's fuel system. However, the relative slow response time of the regular membrane filtration method which was applied to determine the MCL, made it inconvenient for decision making for field operations. A laboratory study revealed that the sensitivities and detection limits of two commercial ATP test kits were within the range required for detecting such MCL levels in Diesel fuel. One of the kits was evaluated for its capacity to be used for rapid in-situ determination of MCL in combat vehicles' diesel fuel tanks, in the field. Preliminary results have shown that a statistical cutoff value of Relative Light Units (RLU), which is specific to the ATP kit in use, can be set as a threshold limit that distinguish between low and high MCLs. Using such an approach, ATP kits may be used successfully to determine the MCL levels that indicate a need to clean Diesel fuel tanks before refueling.

EFFECT OF TEMPERATURE ON THE RATE OF KILL OF ANTI-MICROBIALS FOR AVIATION FUEL

Graham C. Hill, Edward C. Hill, Rachael Ling and Derek J. Collins

Microbial contamination is a sporadic but costly problem in the distribution and use of distillate fuels. Where good housekeeping practices, primarily the control of the ingress and accumulation of water, fail to prevent microbial growth, treatment with anti-microbial chemicals (biocides) is usually prescribed. Where excessive growth occurs, treatment may need to be preceded by tank and system cleaning. The downtime required for treatment of aircraft fuel tanks has a serious logistical and economical impact on operations. Even without tank cleaning, biocide treatment may result in 1 – 4 days of aircraft downtime on account the prolonged soak time required for biocides to be effective. It is known that the kill rate of biocides can be highly temperature dependent. Some biocides are only effective against microbes which are metabolically active because the microbe has to absorb and metabolize the anti-microbial agent in order to realize its killing potential. At temperatures below 4°C most microbes will not be metabolically active, although many will survive in an inactive state at far lower temperatures. Conventional biocide kinetics suggest that many biocides will cease to be effective below 4°C. For this reason biocide treatment procedures for aircraft now stipulate that flight time (when fuel tank temperature is likely to fall considerably below 0°C) should not be included in the prescribed biocide soak time. In the field, biocides are usually applied to aircraft while they stand on the apron, at temperatures which may vary considerably, reflecting the diverse range of climates that aircraft operate within. One might expect that a treatment applied in sub-tropical conditions would be considerably faster acting than a similar treatment applied outdoors in winter in Europe or North America. Application of biocide fuel treatments within the hangar is often not a practical proposition. The benefit of biocide use outdoors at temperatures approaching 0°C has been questioned. Surprisingly little is known about the kinetics and mode of action of many fuel biocides and, to our knowledge, the effect of temperature has never been thoroughly investigated. This study aimed to establish the effect of temperature on the kill rate of 3 commercially available fuel biocides (two of which currently have approvals for aircraft use) and also di-ethylene glycol mono-methyl ether (DiEGME) which has been used and marketed as an anti-microbial agent for aviation fuels.

BACTERIAL CONTAMINATION OF HIGH OCTANE NUMBER OXYGENATED GASOLINE

Tao zhiping and Zhang ji

Since 2001, bacterial contamination of oxygenated gasoline occurred in South China and caused blocked filter, and even more damaged gasoline pump. This bacterial contamination only occurred in high octane number oxygenated gasoline. We investigated that the composition of deposit that blocked filter is 70 percent ferric oxide, environment and climate of storage tank and the eight microorganisms collected from contaminated gasoline tank bottom-water samples. Furthermore, we find microorganism propagated is different between the 90 gasoline and the 97 gasoline. This is caused differ contaminations.

SESSION 9: AVIATION FUELS

AVIATION GASOLINE: HISTORY AND FUTURE

Alisdair Q Clark

Aviation gasoline represents a high-performance fuel developed specifically for spark ignition aircraft piston engines. The product has over eighty years of history where successive engineers and scientists have sought to provide a fuel which will deliver maximum power and range for flight, and be capable of operating in a wide range of climatic conditions from sea level to high altitude. Currently, aviation gasoline Grade 100LL dominates this market, offering a combustion performance and quality far in excess of automotive fuels. However, to achieve this level of performance requires the use of the octane enhancement additive tetraethyl lead, making 100LL one of the last remaining leaded fuels available in the modern world. The Aviation Industry is seeking an unleaded fuel to replace 100LL and take piston engine development into the future. Given the high standard of product required this represents a challenging program. Within this paper a review of current research into unleaded aviation gasoline is provided, reaching back into history to key stages in development to illustrate how quality, performance and engine design have influenced the present fuel, and will in turn, influence the future.

SIMULATIONS OF FUEL TANK TEMPERATURES WITHIN U.S. AIR FORCE CARGO AIRCRAFT AS PART OF A JP-8 REPLACEMENT STUDY

Jamie S. Ervin and Thomas M. Bartsch

Jet A fuel currently offers cost advantages over JP-8 jet fuel. If Jet A could be used to replace JP-8 in cargo aircraft, the U.S. Air Force could potentially realize significant cost savings. Jet A has a higher specification freeze point than does JP-8. Thus, it is necessary to study cargo aircraft and assess the impact of Jet A use on safety and operability. Simulations of the heat transfer within critical fuel tanks were performed using computational fluid dynamics (CFD) and a zero-dimensional model. For model development, the aircraft manufacturers provided information on tank configurations, fuel flow rates, electrical loads, wing characteristics, and thermal properties. In addition, flight tests were performed for model validation. It is challenging to use CFD to calculate the transient temperatures within large fuel tanks for long missions. During tank draining, the use of a relatively large grid with sufficient resolution required small time steps (~0.001 s to 0.04 s) for numerical stability. In spite of complexities, the CFD models provided details of the temperature and flow velocity spatial variation not available with the zero-dimensional model. In contrast, simulations involving the zero-dimensional model required calculation times of only minutes rather than days or weeks as needed for the CFD models. Bulk temperatures calculated by the two methods agreed well with each other. Lastly, the presence of foam in a fuel tank complicates the understanding of the fuel temperature behavior and was difficult to accurately represent in the models.

EFFECT OF “FAME” CONTAMINATION ON JET FUEL THERMAL OXIDATIVE STABILITY

George R. Wilson, III, Pam Serino, Melanie Thom

Fatty acid methyl ester (FAME), commonly known as Biodiesel, is becoming a common blending material for commercial diesel fuel. In the common transport system this generates a potential for the contamination of jet fuel with FAME. The authors have tested these contaminations at both micro and gross levels. In this paper we will discuss both the anticipated negative results of gross contamination but also the measurable effects of contamination at the parts-per-million level.

B10 AND JET A-1 IN MULTIPRODUCT PIPELINES – TRAPIL TRIAL

Patrick Viltart

The content of FAME in diesel fuels is planned to increase in a future in France, as in many other countries. A working group bringing together French Administration, French National Oil Industry Association, Oil Companies and Pipeline Operators was set up in 2006 with the scope to establish the protocol of a trial on the multiproduct pipeline Le Havre Paris, to evaluate the impact of Biodiesel on Jet Fuel. The trial was carried out in April 2007. A 1000 m³ cargo of Jet Fuel pushed a 6500 m³ cargo of Biodiesel containing 10% of FAME through a 20 inch 150 km pipeline. Samples were taken every 25 m³ in the interface and 50 m³ in the Jet Fuel cargo. After the interface, FAME has been identified by 2 independent laboratories at ppm levels in the first 400 m³ of the Jet Fuel cargo by using GCxGC method. No measurable variations of the Check List properties of Jet Fuel were noted, between the samples taken at the entry into the pipeline and the arrival, after the 150 km transfer behind the cargo of Biodiesel. The JFTOT Break Point was found unaffected by the pipeline transfer. The Industry needs to find a way to accommodate Biodiesel transport and Jet Fuel transport in multiproduct pipelines. To discard Jet Fuel which contains trace levels of FAME by increasing the interface volume, is not a cost saving option and might not prove to be practical. It will also reduce the available quantities of Jet Fuel as more Jet Fuel will be downgraded. The way forward is

1) to determine the level of FAME up to which there is absolutely no impact on the suitability for use of Jet Fuel; and 2) For pipeline operators to implement Quality Assurance procedures to guarantee the Jet Fuel delivered does not exceed this concentration in the receiving tank.

STUDY OF THE OXIDATION OF THE MAIN HYDROCARBON FAMILIES CONTAINED IN THE KEROSENE JET A-1

Mickaël Sicard, Christophe Hein, Sterenn Gernigon, Frédéric Ser, Dominique Brodzki, Gérald Djéga-Mariadassou

In modern aircraft, on board fuel is used not only for propulsion but also as a primary coolant. Thus, in the fuel system and injection devices, the fuel temperature can increase significantly. This thermal stress conjugated with the presence of dissolved dioxygen can lead to the formation of gums and solids. These deposits can cause fouling of nozzles and heat exchangers. As kerosene Jet A-1 is a complex blend of hydrocarbons, containing at least 300 components, it is difficult to determine from which hydrocarbons the deposits come from. But, when taking a closer look, all the hydrocarbons can be classified in 3 main families: alkanes (linear and branched), cycloalkanes (mono or bi-cyclic) and aromatics (mono or bi-cyclic). The objective of

this work consists in studying and determining the behaviour under oxidative conditions of, at least, one molecule representative of each hydrocarbon family of the Jet A-1. This study is carried out with a back surge device at 185°C. In order to exacerbate the oxidation reactions, a continuous air flow (100 mL/min) is added to the liquid. Various hydrocarbons are tested as n-dodecane, heptamethylnonane, 1-3 diisopropylbenzene, 2-methylnaphthalene. During a 72 hour test, regular samplings of the liquid and gaseous phases are carried out. They are characterized by GC, GC/MS, HPLC and IR spectroscopy. As expected, the stability towards oxidation is different from one hydrocarbon to another. For example, more than 50% of n-dodecane reacts during the test whereas the quantity of 2- methylnaphthalene does not change significantly. In some cases, gases like H₂, CO₂ and light hydrocarbons are detected. Nevertheless, oxidized products such as alcohols, ketones and carboxylic acids are formed from all the hydrocarbons. Moreover, this study points out which hydrocarbons could lead to the formation of gums and solids since heavier products than the parent hydrocarbon are observed.

SESSION 10: FUELS FROM UNCONVENTIONAL SOURCES

STABILITY AND HANDLING ISSUES ASSOCIATED WITH AVIATION TURBINE FUELS DERIVED FROM BIO SOURCES

George R. Wilson, III

Synthetic fuels present unique challenges for specification writers. We have gone through one iteration of this issue with the development of synthetic fuels from coal and natural gas via the Fischer Tropsch and related processes. Now the emphasis is on developing fuels from bio sources. While it is theoretically possible to reduce bio materials to synthesis gas and end up with the same product as coal derived fuels that approach is economically unattractive. This means the origin of the material has more potential impact on final product. In this paper the author will discuss the issues involved with preparing a suitable aviation turbine fuel from bio sources.

USE OF A SIMULATION MODEL TO EVALUATE THE USE OF VEGETABLE OIL IN A NEW REFINING PROCESS FOR DIESEL USING EXISTING INSTALLATIONS

Cláudio P. Limoeiro, Daniel Barry V. Fuller, Guilherme A. Barbosa, Marcelo G. Tito

The current concern over sustainable development has shown the need to define new limits for automobile emissions. Researchers have been looking for economical, renewable, less polluting fuels. In accordance to this, the H-Bio process was developed. This technology replaces up to 10% of the volume processed to obtain diesel in the refinery with vegetable oil using the currently installed equipments. However, such change has an impact in the storage and handling of the products involved in this process around the tank farms. In order to evaluate this impact, Petrobras has been using simulation models, whose greatest advantage is their flexibility to test parameters and configurations and to foresee the consequences of new stock politics and new processes without the need to actually build or redesign plants. Using the joint analysis of the input parameters and results, it is possible to detect operational bottlenecks, plot comparative graphs and analyse the results of new investments, searching for cost-reducing opportunities and

substantiating technical and managerial decisions regarding stock optimization. In this work, we shall present the application of one such model in a study in Petrobras' largest refinery, which has had to change substantially its storage facilities and diesel-forming process to account for the H-Bio and keep up with the new, stricter environmental restrictions to Brazilian diesel. From the model's output, the number of tanks needed by each product involved was inferred and the best way to schedule the receiving and using of vegetal oil was chosen without restriction introduction.

RENEWABLE DIESEL FUEL

Frederick J. Cornforth, Joseph Kaufman and George Parks

Renewable Diesel is the name given an attractive fuel that moves co-processed hydrotreated biological fats or oils directly through the refinery into the transportation fuels pool, displacing the need for an equal amount of imported crude oil or expanding the available diesel pool without added crude oil imports. Renewable diesel is a clean burning all hydrocarbon ultra low sulfur diesel (ULSD) virtually indistinguishable from conventional crude oil derived ULSD. It will have more cleaner-burning paraffinic hydrocarbons and fewer aromatic hydrocarbons than the base oil with which it was co- processed. Hydroprocessing converts the triglycerides, which compose fats or oils, into the same molecules that are already in the diesel fuel. The process thermally depolymerizes the triglyceride, and then stabilizes the products, eliminating any carbon-carbon double bonds inherited from the fat or oil. Renewable diesel is an eco-friendly fuel that supports the agricultural community while significantly reducing greenhouse gasses. Engine tests have demonstrated reduced regulated NO_x, CO, NMHC, and PM relative to the conventional ULSD with which it was coprocessed. Furthermore, well-to-wheels analysis of the CO₂ emitted over the full life cycle of renewable diesel indicate that renewable diesel fuel will reduce GHG CO₂ by over 55% relative to conventional diesel. All groups that have calculated these life-cycle emissions for both renewable diesel and biodiesel from the same biological source agree that renewable diesel may outperform biodiesel in this regard.

TRANSPORTATION FUEL PRECURSORS FROM UNCONVENTIONAL SOURCES

Parviz M. Rahimi, Craig Fairbridge, Ken Mitchell, Bruce Bunting, Sam Lewis, John Storey, Tom Gallant, James A. Franz and Mikhail S. Alnajjar

Oil sands are a naturally occurring mixture of bitumen, sand, clay and water, containing 10 to 12 wt% bitumen or extra heavy oil, defined as oil with a density greater than 960 kg/m³. In 2004, production of oil sands products was 1 million barrels per day. Several sources project that bitumen derived crude oil production will reach 3 million barrels per day in 2015, and production could reach 5 million barrels per day in 2030. The relative yields of transportation fuel precursors in conventional light petroleum and bitumen derived crude oil are different. Further, oil sands transportation fuel precursors contain more aromatic and cycloparaffinic compounds than corresponding conventional light crude oil products.

From 2005 to 2030, global personal mobility needs will stimulate an evolution of technologies in vehicles, advanced low-temperature combustion engines as well as transportation fuels. This is

motivated by concern for human health and the environment – to reduce criteria air contaminants and to mitigate climate change. The volume of North American transportation fuels derived from oil sands will increase 3 to 5 times in this time period, and future fuels will include increasing amounts of oil sands, bio-renewable, shale oil, and Fisher-Tropsch derived materials. Differences between oil sands products and those from conventional heavy oil are reduced by increased processing severity. Commercial bitumen upgrading to synthetic crude oil includes coking and hydrocracking. In this study, refinery streams from both coked and hydrocracked synthetic crude oil are compared. Analyses indicate the same hydrocarbon classes but detailed information on isomers is not readily available from conventional analyses. A range of analytical data is available on the streams, including C13 and 1H NMR, and FI, CI and EI GC/MS. The chemistry of selected streams will be compared and contrasted.

SESSION 11: POSTER SESSION

FOULING CHARACTERISTICS AND MITIGATION OF SOUR CRUDES

Parviz M. Rahimi, Youngjun David Oh, Remy McNamara, Teclemariam Alem, and Irwin Wiehe

Fouling in refineries during petroleum processing occur when fuels are subjected to temperatures typically around 300°C. Although the amount of fouling is small in a short period, but because of high throughput and the length of time on stream, a significant amount of deposits is formed. The flow restriction reduces throughput and solids formation reduces process efficiency resulting in higher energy cost and overall green house gases (GHG) emissions. Although the mechanism of fouling is complex but the occurrence of fouling in different parts of petroleum processing has some commonality. Deposits are usually formed by; asphaltene precipitation, polymerization of reactive components of the oil and also by impurities such as corrosion products. Most common causes of fouling have been identified as, inorganic solids, oil incompatibility on mixing, coke from over thermal treating, polymerization of olefins and di-olefins, and insoluble asphaltene on cooling after conversion. Once the cause of fouling is identified the mitigation can be developed to reduce or eliminate solids formation. Different chemistries have been developed to reduce process fouling by using anti-foulants. Different laboratory methods and techniques have been developed for measuring fouling rates of petroleum streams. Research on fouling of different crudes has shown that paraffinic crudes with low asphaltene had relatively high fouling rates. More recently work at National Centre for Upgrading Technology (NCUT) showed that a high fouling crude can be stabilized and its fouling rates was reduced by addition of bitumen containing relatively high concentration of resins. The fouling rates were shown to be additive and correlated with the percent of bitumen in the mixture of crude plus bitumen. Results will be presented showing the coking propensity/onset of a highly foulant crude as function of process severity. Further, it will be shown how fouling can be reduced by the addition of bitumen containing high concentration of aromatics and resins.

DETERMINATION OF MERCURY IN CRUDE OIL USING A NOVEL METHOD

Stephen E. Long, W. Robert Kelly, Jacqueline L. Mann, and Harry N. Giles

A high-accuracy analytical method employing isotope dilution combined with cold-vapor generation inductively coupled plasma – mass spectrometry (ICP-MS) has been used to determine mercury in more than 100 crude oil and 29 sludge samples from the DOE Strategic Petroleum Reserve (SPR) and other sources. The mercury in the sample is converted to free Hg²⁺ ions using nitric acid in a closed system combustion process employing Carius tubes. This process ensures complete equilibration of the isotopic spike (²⁰¹Hg) and the mercury in the sample and, at the same time, eliminates the possibility of external contamination and volatilization loss. Determination by isotope dilution ICP-MS is absolutely specific for mercury and provides superior sensitivity and accuracy. The method detection limit for mercury in crude oil is 0.02 ng/g and is limited by the analytical blank. All samples analyzed were above the detection limit, but most crude oils were very low: 77 samples (75 %) were below 1 ng/g Hg and 90 samples (87 %) were below 2 ng/g Hg. The grand mean for 103 crude oils was 1.4 ng/g Hg (1s = 2.8 ng/g). In addition to the SPR samples, the method has been used to determine mercury in several Canadian samples and in Cymric, a crude oil previously reported to contain extremely high levels of mercury. The Hg concentration in sludge samples ranged from 2 to 500 ng/g

HYDROCARBON LIQUID FUELS THERMAL STABILITY, ANTIOXYDANT INFLUENCE AND BEHAVIOUR

Stérenn Gernigon, Adrien Aubourg1, Mickaël Sicard, Frédéric Ser, François Bozon-Verduraz

Jet fuel undergoes oxidative chemistry upon being heated in the fuel systems of advanced civil aircraft. The degradation process may lead to the formation of bulk and surface solids in the fuel system. Deposits formation has different origins; one of them is the dissolved oxygen which initiates formation of peroxides. The aim of this study is to strongly decrease or inhibit the oxidation reactions present during the fuel degradation. This is why the use of antioxidant additives is considered. In order to study these reactions, oxidation is exacerbated by the use of a back surge device. Liquid fuel is stressed to a bulk temperature of 185°C with an air flow of 100 mL/min. Kerosene is a complex blend of hydrocarbons, approximately 300 species, so we used one of its major components, the n-dodecane n-C₁₂H₂₆, as model. The characterization of the various products (gas and liquid) formed during degradation allows to know the role played by n-dodecane in the degradation of kerosene. Characterization techniques which have been used are GPC, HPLC and IR Spectroscopy. During a 72 hours test, more than half of the n-dodecane is consumed. This degradation involves the formation of different gases like CO, H₂ and light saturated and unsaturated hydrocarbons. The liquid analysis shows the formation of oxidized products like ketones and alcohols. Moreover, there is no deposit formation. Three antioxidants have been tested on the n-dodecane: the phenol, 2, 6-bis (1, 1-dimethylethyl)-4-methyl- (BHT), the phenol, 2- (1, 1-dimethylethyl)-4-methyl- (TBMP) and the phenol, 2, 4-bis (1, 1-dimethylethyl) (2, 4 DTBP). The quantity added to hydrocarbon is about 1% (wt). The n-dodecane quantity remains constant with the use of BHT. The latter is consumed in the place of the hydrocarbon according to a linear law. In the first hours, the addition of TBMP or 2, 4 DTBP slightly reduces the rate of n-dodecane degradation. When TBMP and 2, 4 DTBP are completely consumed, the n-dodecane concentration sharply decreases, faster than without antioxidant. BHT is the most performant antioxidant tested because it protects the hydrocarbon from the degradation during 72 hours, whereas TBMP and 2, 4 DTBP protect n-dodecane less efficiently and only during 24 hours.

DETERMINATION OF THE OXIDATION STABILITY IN BIODIESEL AND BLENDS PROBLEMS AND SOLUTION

Thomas Jebens

The oxidation stability is an important fuel property to describe the ageing behaviour of fuels. Effects of limit transgression in the case of bio-diesel are filter backfill, precipitation of polymers in diesel / bio-diesel mixtures throughout the fuel supply system. In the European EN 590 Standard the ageing behaviour of diesel is characterized by determining the polymer (sludge) content of artificially aged fuel (EN 12205 / ASTM D 2274). Test methods for measuring only the sludge forming potential are unsuitable and do not characterize the oxidation stability in a sufficient way. This Poster shows a new valuable test method for evaluating the oxidation stability in determining the Induction Period with Petrotest new instrument PetroOxy. In a small sealed test chamber, a sample of 5 ml and pure oxygen at 700 kPa is heated up to 140°C. This initiates a very fast oxidation process that is displayed at the end by a pressure drop of 10% in the system. It was found that the time consumption to the pressure drop is directly related to the oxidation stability of the fuel sample. Besides Biodiesel, the PetroOxy is also applicable for Diesel and diesel / biodiesel blends. Several test were made for biodiesel and biodiesel blends and the results are shown on the poster comparing with the existing Rancimat method (EN 14112). Additionally, the PetroOxy method has the advantage to measure quick and directly the oxidation stability and is an ideal tool for process and test bench control.

DETECTION AND CHARACTERISATION OF UNDISSOLVED WATER AND PARTICULATE IN JET FUEL

Garry K. Rickard

Particulate contamination in jet fuel is normally assessed by gravimetric Millipore testing (IP 423 / ASTM D 5452). This test method has a number of disadvantages, such as poor precision, large sample size and it is not possible to gain real time results. In recent years, the use of particle counting technologies have been investigated and two laboratory based methods are available from the Energy Institute. The methods are based on laser obscuration technology. This technology has been used for other petroleum products for many years and has a number of advantages over the gravimetric methods such as, smaller sample size, analysis time, technology transferable through distribution chain (on line real time analysis available), calibration to ISO standards. Due to the success of the laser obscuration methods in identifying contaminants in jet fuel other particle counting devices have also been investigated. This paper/poster shows an initial investigation into the detection and characterisation of particulate and water in jet fuel using a video microscope. A number of different parameters including concentration; size, shape, and optical density are investigated as tools to characterise particulate and water in jet fuel.

THE IMPACT OF A SELECTION OF FATTY ACID METHYL ESTERS ON JET FUEL QUALITY

Peter S Brook and Garry K Rickard

Two examples of jet fuels from UK sources, one hydrotreated, the other Merox, were blended with a range of fatty acid methyl esters, FAMEs, from different biological origins. The level at which the FAMEs could be detected by specification test methods varied with property and FAME type. Low concentrations of some FAMEs were found to have significant impacts on jet fuel quality.

EVALUATION OF A MODIFIED EN 14112 (RANCIMAT TEST) FOR ASSESSING OXIDATION STABILITY OF BIODIESEL BLENDS

Steven R. Westbrook

Standard Test Method EN 14112, more commonly known as the Rancimat, is the most widely used and accepted test for the oxidation stability of biodiesel (B100). This test method is also being suggested as a means to evaluate the oxidation stability of biodiesel/petroleum diesel blends. Unfortunately, the standard Rancimat test is not well suited for this application and is prone to producing misleading results. Under the standard test conditions, some of the petroleum fraction can begin to distill. The petroleum vapors can create materials incompatibility problems with some of the test equipment (i.e. plastics and elastomers). The petroleum can also interfere with the conductivity measurements taken by the instrument. The instrument manufacturer has developed test modifications to address these incompatibilities and make the test applicable to blends. This paper presents the results of many Rancimat tests of biodiesel/petroleum diesel blends. The blends were tested using both the standard test method and the revised method. Tests were conducted on two separate instruments. Many of the blends were also tested by other stability tests and the results are compared as a measure of the test method correlations.

EFFECTS OF AROMATIC TYPE AND CONCENTRATION IN FISCHER-TROPSCH FUEL ON EMISSIONS PRODUCTION AND MATERIAL COMPATIBILITY

Matthew J. DeWitt, Edwin Corporan, John Graham and Donald Minus

There has been continued interest in the potential use of fuels produced via the Fischer-Tropsch (FT) process for aviation applications. These fuels can be produced from various non-petroleum feedstocks, such as coal, natural gas and biomass, and could reduce reliance on foreign supply. FT fuels are typically comprised solely of iso- and normal-alkanes and do not contain aromatics or heteroatoms. These latter compounds are believed to provide seal-swell and other needed fit-for-use properties, but have also been shown to increase undesirable particulate matter (PM) and gaseous emissions during combustion. The eventual widespread use of FT fuels may require blending with an additional feedstock to provide specific operational properties. One potential option is to blend with an aromatic solvent. An improved understanding into the effect of the type and concentration of the aromatic solvent on overall system performance will assist in identifying potential candidates to meet the operational requirements. Of specific interest are the extent by which the combustion emissions and seal-swell behavior will be affected. In this effort,

three different aromatic solvents of varying molecular weight encompassing the range found in typical JP-8 fuels, were added both independently and as a blend to an FT fuel to assess their effects on the emissions of a T63 engine and on seal swelling. The engine was operated at two power conditions, idle and cruise, to study the effects of varying combustion temperatures and pressures. Strong impacts on the emissions were observed as a function of both the solvent type and blend concentration used. Improved swelling characteristics of nitrile rubber O-rings were observed with addition of the aromatic solvents. Test procedures, analysis techniques, and results will be presented.

A MICROBIOLOGICAL EXAMINATION OF A BIODIESEL SAMPLE OVER TIME

Capt Sarah K.C. Brooks, Ellen M. Strobel, Loryn L. Bowen, Marlin D. Vangsness, Lori M. Balster, and Susan S. Mueller

This poster details a year-long study of the microbial contamination found in a single sample of B-20 using microbiological and molecular techniques. Biodiesel is a domestically produced, renewable fuel that can be manufactured from vegetable oils (the least expensive of which is soy oil), animal fats, or even recycled restaurant greases. B-20 is more specifically a blend of 20% B100 and 80% diesel and can be used in diesel engines without modification. The United States Air Force uses B-20 at several CONUS locations to supplement the diesel supplies for ground power applications. An ATP measurement was made and filtered microbes were archived on FTA paper on site within two hours of sample capture. Fuel was also sent to the laboratory at Wright Patterson Air Force Base where it was cultured on multiple types of media as well as processed via non-culture methods (PCR). Over a period of one year, five test points were accomplished where the biodiesel sample was re-cultured and PCR to observe consortia changes over time. Initially, growth was prolific on several types of media and several fungal and bacterial species were identified. Initially, fungi were the dominant species but bacterial species became dominant as time progressed. Sequencing of the 3 week, 6 week, and 3 month time points showed a varying amount of bacterial populations present in the biodiesel. By the 6 month time point, growth on culture medium had been reduced significantly with no fungi present and only a few bacterial species growing which were predominately Gram positive cocci.

FISCHER-TROPSCH IPK ASSESSMENTS OF FIT-FOR-USE IN THE ARMY'S TACTICAL GROUND VEHICLES

Patsy A. Muzzell, Luis A. Villahermosa, Brian J. McKay, Eric R. Sattler, and Leo L. Stavinoha

The U.S. Army's Tank Automotive Research, Development and Engineering Center (TARDEC) has completed several evaluations of Fischer-Tropsch Iso-Paraffinic Kerosene (FT IPK) to assess fit-for-use (i.e., suitability for use) in Army tactical ground vehicles. As this fleet is primarily powered by heavy-duty diesel engines, and these engines must be capable of powering heavy vehicles in extreme environments under severe duty cycles, alternatives to current JP-8 fuel must include consideration of these demanding requirements. In addition, alternatives should be freely interchangeable with JP-8 to accommodate worldwide deployments; unlike JP-8 generally available and widely produced throughout the world, the availability of alternatives would likely be of limited volume for many years yet and not be nearly as globally produced. The FT IPK

evaluated is comprised of hydrocarbons in the kerosene range (mostly C9 – C16), is very “clean-burning” in that it contains no aromatics, no sulfur, and is free of various trace compounds typically found in petroleum fuels; the FT IPK has a high cetane number (about 60), and a high temperature viscosity that meets the minimum (1.3 mm²/s at 40°C) for No. 1 diesel per ASTM D975. On one hand, these attributes define a high performance diesel fuel, while on the other they require that the FT IPK be assessed adequately. The FT IPK has a somewhat lower density than the minimum called out in the JP-8 specification (0.754 kg/L vs. 0.775 kg/L), a slightly lower volumetric energy density than typical JP-8, and less inherent lubricity than petroleum fuels. In addition, the FT IPK has lower solvency than petroleum fuels, resulting in possible sealing concerns in fuel distribution systems, but only for some types of sealing applications and some types of fuel-wetted elastomer materials (primarily nitrile). TARDEC evaluations have focused on two of the most critical areas: elastomer compatibility and fuel lubricity. Assessments show FT IPK fuel lubricity can be significantly improved by current military- specified lubricity improver additives, and that one means to address elastomer compatibility is by the use of blends of FT IPK with JP-8. TARDEC’s study of blend properties shows significant quantities of FT IPK can be blended in JP-8 typical of U.S. supply, while still meeting an existing specification precedent for similar blends; namely up to 50% V FT IPK from Sasol’s Secunda, South Africa plant with Jet A-1, found acceptable for commercial aviation use.

REDUCING THE ARMY’S DEPENDENCE ON OIL: FUELING TACTICAL GROUND VEHICLES WITH AN “ASSURED FUEL” ALTERNATIVE TO JP-8

Patsy A. Muzzell, Eric R. Sattler, and Leo L. Stavinoha

JP-8 / JP-5 aviation kerosene-type fuel is the bulk fuel used in all Army, Air Force, and Navy tactical fleets; JP-8 / JP-5 fuel is in essence the same as the predominate fuel, Jet A-1, in use by the commercial aviation industry worldwide. The U.S. Army Tank Automotive Research, Development and Engineering Center (TARDEC) is actively engaged in a drive to develop freely interchangeable fueling alternatives to JP-8 / JP-5. This drive is part of a larger campaign in the U.S. Military, and an even larger effort throughout the U.S., to reduce dependence on petroleum crude oil. When it comes to fuels critical to the mobility of the military, industrial, and civilian sectors, aviation kerosene fuel, (a.k.a., jet fuel) is one of the most critical. Commercial large-scale production of jet fuel in the U.S. from domestic, non-petroleum resources can play a significant part in “kicking our addiction to oil” and creating an “assured fuels” supply. The Army has 39 Forts located within the Continental United States (CONUS), at which tactical vehicles, of various types and numbers, are fueled with JP-8. These vehicles must be ready at all times for use in national defense and worldwide deployments. Not just any fuel will suffice to ensure these vehicles, most powered by heavy-duty diesel engines, can meet demanding readiness requirements and mission profiles. One type of fuel with good high- performance diesel properties and potential to become an “assured fuel” alternative to JP-8 is Fischer-Tropsch (FT) Iso-Paraffinic Kerosene (IPK). A realistic implementation path is to convert to the use of blends of FT IPK with JP-8 in tactical vehicles at CONUS Forts. A recent study by TARDEC looks at a subset of the Army’s Forts in CONUS based on JP-8 fuel usage and distribution among the five CONUS Petroleum Administration for Defense Districts (PADDs). Five Forts were selected, one in each PADD, that use comparatively significant volumes of JP-8. The study examines the commercial potential for production of FT IPK in each PADD, the nature of the

current JP-8 fuel supplied to each Fort, and the nature of the fuel produced by blending each Fort's JP-8 supply with FT IPK.

EFFECTS OF POTENTIAL ADDITIVES TO PROMOTE SEAL SWELLING ON THE THERMAL STABILITY OF SYNTHETIC JET FUELS

Dirk D. Link, Robert G. Gormley, Paul H. Zandhuis, and John P. Baltrus

Synthetic fuels derived from the Fischer-Tropsch (F-T) process using natural gas or coal-derived synthesis gas as feedstocks have drawn increased interest as replacements or supplements to petroleum-derived liquid fuels for the powering of ground vehicles, aircraft and ships. The increased attention being given to F-T fuels is because of the associated benefits of reduced dependence on petroleum feedstocks and less impact on the environment due to reduced emissions. Because of their chemical and physical properties, F-T fuels will probably require additives in order to meet specifications with respect to lubricity and seal swell capability for use in ground and air vehicles. These additives can include oxygenates and compounds containing other heteroatoms that may adversely affect thermal stability. In order to understand what additives will be the most beneficial, a comprehensive experimental and computational study of conventional and additized fuels has been undertaken. The experimental approach includes analysis of the trace oxygenate and nitrogen-containing compounds present in conventional petroleum-derived fuels and trying to relate their presence (or absence) to changes in the desired properties of the fuels. In the short term, potential problems associated with seal swelling may be mitigated by blending conventional fuels with synthetic fuels to maintain the levels of active compounds above the necessary threshold. In the long term, the problem will likely be solved by adding components to synthetic fuels that allow better compatibility with existing fuel systems. This presentation will describe the results of efforts to test the thermal stability of mixtures of synthetic and petroleum-derived fuels as well as synthetic fuels containing single-component additives identified in earlier research as the best potential additives for promoting seal swelling in synthetic fuels.

RENEWED STORAGE STABILITY LIMITS FOR JET A-1 BEING USED BY INDIAN AIR FORCE

S. Nandi, R. Manoharan, V. K. Sharma, A. A. Gupta & R. K. Malhotra

Jet A-1 is a kerosene grade of fuel suitable for most turbine engine based aircraft. It is produced as per stringent internationally agreed standard with flash point above 38°C (100°F) and freeze point of -47°C maximum. Jet A-1 meets the requirements of British specification DEF STAN 91-91 (Jet A-1), (formerly DERD 2494 (AVTUR)), ASTM specification D1655 (Jet A-1) and IATA Guidance Material (Kerosine Type), NATO Code F-35. Jet A-1 fuel is used for fueling both civilian and military aircraft. Storing of Jet A-1 fuel in storage tanks for 30 to 45 days for civilian aircraft is not an issue, since all the fuel meant for storing is consumed within the stipulated time. However, it is a serious problem when stored for more than a year, as practiced for storing Jet A-1 fuel for fueling military aircrafts. Fuel stored for a longer time gives rise to instability in which hydroperoxides and peroxides are the initial reaction products. These products remain dissolved in the fuel and shorten the life of some fuel system elastomers. Also

additional reactions results in the formation of soluble gums and insoluble particulates. These products may clog fuel filters and deposit on the surfaces of aircraft fuel systems thereby restricting flow of fuel to engine. Under Indian context, Jet A-1 is certified for first six months and then every three months recertification is done provided the fuel meets the full specification when tested as per Def Stan 91-91/1 Derd 2494, for Aviation Turbine Fuel Kerosine Type, Jet A-1. In order to study the enhances service life of Jet A-1, a comprehensive research programme was initiated at IndianOil R&D Centre. Three refineries were identified and for collection of the fuel samples, epicoated containers were specially made and sampling was done as per as per ASTM D-4057 procedure. A systematic study was taken up for predicting the renewed storage stability limits of JETA-1 Fuel. A set of ATF samples from the three refineries were evaluated at zero day, six months, twelve months, eighteen and twenty four months of storage, as per Def Stan 91- 91/1 Derd 2494, for Aviation Turbine Fuel Kerosine Type, Jet A-1.