8^{TH} INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS
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Abstract Summaries

Keynote Address:

REDUCING EMISSIONS AND ITS IMPACT ON THE AVIATION INDUSTRY

Joseph Stoneciper, Clifford A. Moses, Russell Strong, and Collin Cross

The environmental impact of emissions generated by transportation fuels are becoming more critical and influencing everything from fuel quality to the types of vehicles we drive, and maybe someday fly. As an example, in 2006 the EPA has mandated the use of ultra low sulfur diesel that dramatically lowers the sulfur content in No. 2 highway diesel fuel in an effort to reduce the emissions in future years. While these mandates do not have a direct impact aviation fuels, the global goal of reducing emissions is expected to ultimately impact decisions in the aviation industry as air travel increases in both developing countries and established economies.

This paper is part of an ongoing project designed to look at the impact of aviation fuel quality in terms of fuel composition in combination with fuel additives on gas turbine emissions using a 3-cup sector rig constructed from a GE T700 engine at Southwest Research Institute. The following variables are examined:

- Particulate Concentration
- Particulate Size and Distribution
- Gaseous Emissions (HC, NO_X, CO_X, CO, etc.)
- Polyaromatic Hydrocarbons (PAH)

Phase I of this work focuses on a GE Betz fuel additive developed as part of the USAF JP-8+100 Program, SPEC•AID 8Q462, at a single concentration level in conjunction with two commercial JET-A fuels.

SESSION 1: GREEN FUELS

BIODIESEL AND BIODIESEL BLEND PROPERTIES RELATED TO EPACT USE

Leo L. Stavinoha, Emilio S. Alfaro, Jill M. Tebbe, and Luis A. Villahermosa

Biodiesel is “a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats, designated B100” in the American Society for Testing and Materials (ASTM) D 6751 specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels. In 1992, the Environmental Protection Agency (EPA) enacted the Energy Policy Act (EPAct) requiring federal and state vehicle fleets to purchase alternative fuelled vehicles (AFV). EPAct was amended in 1998 as the Energy Conservation and Reauthorization Act (ECRA) to include biodiesel as an option for meeting AFV acquisition requirements by purchasing and using either 450 gallons of biodiesel or 2250 gallons of a biodiesel blend consisting of 20% volume biodiesel in petroleum diesel fuel designated as B20. An effort to provide a specification for B20 biodiesel blended fuel for use by government agencies resulted in publication of CID A-A-59693, Diesel Fuel, Biodiesel Blend (B20). This report summarizes data developed to characterize biodiesel samples (identified in market survey, TARDEC Technical Report No. 13801) and biodiesel (B20) blends. The biodiesel feedstocks included unused soybean oil, used cooking oil, used soybean cooking oil, unused vegetable oil, used vegetable oil, unused canola, unused cottonseed, and yellow grease. The data was instrumental in deciding that the B20 specification should be restricted to one grade of biodiesel blend as the winter grade LSD1 has too restrictive of a distillation requirement. The B100 samples were also tested for oxidation stability in accordance with ASTM D 6186, Standard Test Method for Oxidation Induction Time by Pressure Differential Scanning Calorimetry (PDSC), at 130°C. The biodiesels having the highest level of unsaturation were the most reactive but ranged considerably depending on source. Biodiesel from used feedstock and all B20 blends did not have measurable induction times at the selected test temperature and are considered to be more oxidatively stable than the soy based biodiesels that had measurable induction times below 120 minutes.

REDUCED SULPHUR AVIATION FUELS – A WORLDWIDE CHALLENGE

Joanna M Bauldreay and Charn-Hsiang Ang

Automotive fuels with increasingly low sulphur levels are mandatory in numerous countries. Early sulphur reductions directly benefited the environment (improved air quality and reduced engine emissions) while later ones produce indirect benefits; enabling technologies can further reduce nitrogen oxides or particulate emissions from exhausts.

Kerosine, for jet fuel, distils between gasoline and diesel and accounts for about 10%v of the barrel. It has not yet followed suit on the downward trend on sulphur. In most countries the maximum sulphur level is 3000 parts per million by weight but the global average sulphur level is significantly below this. Many feel that aviation fuel sulphur levels should not be so different from those of ground fuels. The industry debate has opened and jet fuel specification writers are proposing that the maximum soon be dropped to at least 2000 ppm, more to prevent actual jet fuel sulphur levels from rising than for proven advantages to the environment. Should convincing data become available showing that further sulphur reductions would benefit the environment, lower maxima may subsequently be proposed. From a US or European perspective, this first change should not be too problematic. This may not be the more global position. This paper will overview benefits and concerns related to reducing jet sulphur levels. It will identify challenges for fuel producers, including issues associated with lubricity. Reflecting how readily or not the world’s refiners could accommodate change, these data should provide valuable insights for specification setters.

POSSIBILITIES FOR THE PRODUCTION OF BIOFUELS AND THEIR STORAGE STABILITY

Slavi K.Ivanov

The protection of the environment and human health puts forth stringent demands to the contemporary fuels - their composition should be free of components causing the appearance of harmful emissions: SO_x, NO_x, polycyclic arenes, alkenes, active oxygen forms (ozone, singlet oxygen, peroxides), soot, metal-containing aerosols, oxygen-containing organic compounds, etc. Recently particular attention is directed to the problems of the green house effect. For this purpose, emission limits for CO_2 are implemented. These problems can be solved by using ultra-clean fuels for internal combustion engines. This type of fuel does not practically contain sulphur (below 10 ppm/l), the aromatics in the diesel fuels is reduced to below 11 vol. %, and in gasoline - below 35 vol. %, the content of benzene and alkenes is limited to 1 and 18 vol. %, respectively, the content of oxygen-containing compounds is also reduced. In addition, the implementation of efficient systems for complete fuel combustion results in removal of some definite noxious emissions such as hydrocarbons, oxygen-containing compounds and NO_x. The production of ultra-clean modern fuels requires large investments in the oil processing industry. It should be also noted that their performance does not automatically lead to complete reduction of CO_2 emissions. For this reason, other ways for the reduction of emissions during the exploitation of the internal combustion engines are also looked for. Applying biofuels and alternative fuels nearly complete absence of SO_x emissions, particles and soot, and reduction in polycyclic arene hydrocarbons emissions, is achieved. The use of biofuels - methyl esters of high carboxylic acids of plant origin and of molasses ethanol - does not affect the CO_2 balance in the atmosphere. The exploitation of liquefied gas propane/butane and pressurised natural gas - methane leads to decrease of the relative fuel consumption and correspondingly to the CO_2 emissions. A particular attention is paid to the stability of the biofuels and other alternative fuels during their storage and exploitation. It is known that the esters of nonsaturated carboxylic acids are particularly unstable and unresisting to the action of light, catalytic systems and the presence of atmospheric oxygen. The use of alcohols causes also problems both with the fuel storage and their specific action on the combustion units in the internal combustion engines. Some possibilities for the increase of the biofuels stability through their chemical modification or by applying special additives are discussed.

SESSION 2: FUNDAMENTAL SCIENCE & MODELLING I

INHIBITION OF JET FUEL DEPOSITION WITHIN A COMPLETE OXYGEN CONSUMPTION REGIME

Matthew J. DeWitt, Steven Zabarnick, and Jamie Ervin

Jet fuel is used both as the propellant and the primary coolant for many aircraft. For current systems, the fuel can provide adequate heat-sink to meet the necessary cooling requirement without chemical reaction of the parent fuel. However, next-generation propulsion systems are expected to reject significantly higher heat loads, which will result in large increases in both the bulk and wetted-wall temperatures that the fuel will experience. This increased heat-flux poses a significant problem since current fuels (e.g.; JP-8) can begin to thermally oxidize and form undesirable carbonaceous deposits at temperatures as low as 150°C. This deposition can result in both the increased maintenance and the possible mechanical failure of the aircraft. Due to these concerns, efforts are underway to develop and evaluate both model and proprietary additives that will enhance the high temperature (> 285°C bulk fuel temperature) stability of standard aviation fuels. These studies are being conducted under a regime where there is complete consumption of the oxygen that is dissolved in the fuel (~70 ppm); which is the condition where the highest amount of oxidative deposition is expected. The experimental methodology employed and results obtained from on-going flow reactor studies will be presented and future research plans will be discussed.

COMPUTATIONAL MODEL OF THE FREEZING OF JET FUEL

Jamie S. Ervin and Daniel Atkins

At high altitudes or under severe environmental conditions, jet fuel may freeze within an aircraft fuel tank. For proper fuel system design, it is important to understand how a fuel freezes and to have the ability to predict where the fuel solidifies. A computational fluid dynamics model is described that predicts the freezing of jet fuel in a buoyancy-driven flow. The model uses measured values of specific heat, viscosity, and density. In addition, the initial normal alkane distribution of the fuel is measured by gas chromatography. Flow visualization experiments are performed using an optical cell together with cross-polarized light. Walls of the optical cell are cooled below the pour point temperature of the fuel. Images of freezing fuel and temperature measurements are recorded using different thermal boundary conditions and fuel samples. The validity of the computational fluid dynamics model is demonstrated by the reasonable agreement between the measured and predicted areas of frozen fuel. In addition, numerically simulated fuel temperatures compare well with measured fuel temperatures.

INVESTIGATION OF THERMAL STABILITY OF HEAVY FUEL OIL BLENDS AND THE EFFECT OF STABILIZING ADDITIVES USING KINETIC LIGHT TRANSMISSION MEASUREMENTS

Åsa T. Håkansson, Jenny-Ann E.M. Östlund, and Margarita Khoklova.

Phase separation of a heavy fuel oil blend (10% residual fuel and 90% visbreaker tar) was investigated, upon addition of n-heptane, using transmission measurements. An optical scanning device that operates by measuring the change in transmission through a diluted fuel oil sample with time was used for the analyses. The results were used to calculate an instability index. That is, a high instability index can be correlated to fuel instability problems. Hence, the effect of stabilizing additives on heavy fuel oil blends and the thermal stability of the oils (with and without additives) could be investigated. Two stabilizing additives (S1 and S2), and one stabilizing additive in combination with a combustion catalyst (SC1) were investigated. The thermal stability of the fuel oil blend was investigated by placing the samples in a heating furnace, at 80°C and 120°C. The samples were analyzed every 24 hours. The results showed that the instability index increased with time during heating. This was observed at both 80°C and 120°C. However, it was shown that the increase in instability index occurred after less time at 120°C compared to 80°C. Addition of stabilizing additives improved the stability of the fuel oil blend in all cases. However, it could be seen that the instability index increased slowly using S1.

SESSION 3: ENVIRONMENTAL & HANDLING

ENVIRONMENTAL IMPACT ON WASTE SYSTEMS CONCERNING THE DISPOSAL OF WATER BOTTOMS CONTAINING THE ACTIVE BIOCIDE INGREDIENT ISOTHIAZOLIN

Howard L. Chesneau

Over the past several years increasing use of Isothiazolin containing biocides in jet fuel has raised concerns pertaining to the disposal of fuel storage water bottoms. In addition, concerns over partitioning ratios in various fuel to water situations has been raised. This paper will address the issues of water bottoms that contain biocides and their impact on water treatment facilities. The partitioning of Isothiazolin active ingredients and dipropylene glycol will also be discussed.

RETROACTIVE FIRE AND EXPLOSION RISKS MANAGEMENT OF CRUDE OIL CARRIERS.

Georgi K. Botev, Zhetcho D. Kalitchin.

A considerable part of the crude oil is transported to the stockpiling reservoirs by tankers. The latter are containing tens and in many cases hundreds of thousands of tons of crude oil. The amount of the crude oil on the tankers is also a threat to the environment in case of an accident leading to crude oil spill. The authors make an analysis of explosions and fires in tankers, carrying crude oil and suggest important conclusions and measures that must be taken for avoiding such accidents. The data analyzed includes the composition of the crude oil, chemical composition of the sludge, tanks' design, violation of the safety and maintenance instructions, level of the risk management and loss control instructions. The efficiency of operational control against sludge accumulation is evaluated in order to be determined its effect on the storage stability. The alteration of crude oil composition and properties has effect on the sludge formation, which are related to the fire safety.

APPLE JELLY CONTAMINATION IN AVIATION JET FUEL STORAGE AND DISTRIBUTION SYSTEMS

J. Andrew Waynick, Steven R. Westbrook, Lindsey Hicks, and Pamela Serino

The objective of this project was to characterize the aviation fuel contaminant known as "apple jelly" with respect to the compositional and process conditions required for its formation, and to determine possible methods, both compositional and process, whereby its formation can be reduced or prevented. The project team conducted 31 separate site visits to collect information and samples. Samples were also collected from sites other than those visited. SwRI received a total of 139 samples consisting of apple jelly, fuel, and other types of samples related to apple jelly contamination. Samples were analyzed for a number of compositional, physical, and chemical properties. The test results were analyzed to determine data relationships and information regarding the various properties of apple jelly. Based on these analyses, examples of both thin and thick apple jelly were synthesized in the laboratory. The synthetic apple jellies exhibited physical and chemical properties consistent with samples from the field. This work demonstrated that apple jelly is a complex mixture. It begins with water and fuel system icing inhibitor (DiEGME.) This mixture reacts with its environment, extracting and dissolving compounds from the materials with which it comes in contact. Some of these extracted compounds react with the water/DiEGME; some react with other extracted compounds or even compounds in the environment that are not in the water/DiEGME matrix. The results explain the majority of the properties of the various apple jelly samples received.

FUEL FILTER WEAR INDEX TEST METHOD

Gary Bessee

Previous research has been presented detailing the development of a new fuel filter test method that incorporates on-line particle counting, diesel fuel, real-world temperatures, and real-world vibration into the test method. This new, novel test method is called the Wear Index Test Method. At previous technical conferences, data was presented detailing the research performed on the Cummins test engine. All those evaluations were suction-side applications. This paper will present the results from the pressure side testing using a Caterpillar 3406E test engine, illustrate the test result differences with and without vibration, repeatability results and the results of peer review.

SESSION 4: THE SUPPLY CHAIN

PETROLEUM STOCKPILING – ITS HISTORY AND AN OVERVIEW OF TECHNOLOGIES AND GLOBAL PROJECTS

Harry N. Giles

The events of September 11, 2001, focused new attention on the importance of strategic petroleum stockpiles. Prior to that date, many countries had stockpiles or stockpile programs that relied on commercial inventory being available during a supply disruption. Since then, some of these countries have begun increasing the size of their reserves, and others have started the development of a stockpile. Stockpiling of petroleum in the western world dates to 1938, when the looming specter of world war prompted the British government to begin building buried tanks for reserves of aviation gasoline. Similarly, stockpiles of gasoline and middle distillate fuels were developed in Sweden beginning about 1940 and continuing throughout the decade; although, cavities excavated in rock were used for these reserves. These early projects were fairly modest in size compared with some of today's petroleum stockpiles. The advent of large-scale stockpiling is dates from 1956, when the British government responded to the Suez crisis by constructing solution-mined cavities in bedded salt near Chester, England for crude oil storage. A further expansion in worldwide development of petroleum stockpiles took place in 1966, when South Africa began storing crude oil in converted coal mines. In 1969, France commenced a program utilizing a converted iron mine and solution-mined cavities in salt; followed, in 1971, in Germany by construction of solution-mined cavities in salt for stockpiling of crude oil. Not until after the oil crisis of 1973-74, however, did the United States begin a strategic petroleum reserve program. Many of these projects have been expanded and now include other products and means of storage, increasing their versatility to respond to differing interruption scenarios, and contributing to greater storage security and integrity. Today, numerous other countries including Finland, Norway, Denmark, Japan, Italy, the Netherlands, Switzerland, South Korea, and Saudi Arabia are known to have petroleum stockpiles. These reserves may be government-owned, company-held, or both. A number of different technologies have been used for stockpiling of petroleum reserves. These include aboveground and buried tanks, floating vessels, converted mines, and specially-constructed cavities in rock. Worldwide, there is now a documented strategic storage capacity of over 200 million m^3 in tanks or rock cavities ranging from under 5,000 m^3 to more than five million m^3. Regardless of the mode of storage or the size, three principal factors will affect the extent to which degradation in quality of stored petroleum will occur, namely: instability, incompatibility, and contamination. Among the problems encountered in petroleum stockpiling projects are biodeterioration, oxidative degradation, sludge accumulation, and buildup of gases naturally occurring in enclosing rock formations.

A FIELD SURVEY OF HEATING OIL PROPERTIES AND FUEL PERFORMANCE – PROBLEMS AND SOLUTIONS

Wai-Lin Litzke, David A. Daniels, E. Beal, and C. Papastrat

A stable fuel with consistent quality is essential for reliable, efficient operation of modern heating systems. One of the oil-heat industry's highest priorities is to reduce the unscheduled service calls that occur in between scheduled maintenance intervals. These no-heat calls, which can account for over 20% of the total number of service calls can be attributed to inconsistent fuel product, fuel degradation and contamination. There is very little information from the field correlating fuel properties with system performance. The National Oilheat Research Alliance (NORA) is sponsoring the first, in-depth study on burner fuels to assess the magnitude and impact of fuel quality on residential heating system performance. With cooperation from fuel oil retailers, an extensive fuel sample collection and analytical effort provided information on the fuel's stability, physical and chemical characteristics from retailer bulk storage terminals to the consumers' tanks. More than 90 samples were manually collected from four retail distributors located in the northeast and mid-Atlantic regions of the U.S.

This paper provides a summary of the results to date on the most important fuel properties affecting fuel performance in residential heating systems. The findings of the survey indicate that poor stability, and contamination with sediment and water (BS&W) are the leading causes of sludge build-up, filter plugging and burner shutdown. Practical tools for the oil-heat industry are now being developed to evaluate the most cost-effective means to substantially improve fuel quality and performance in the field.

SESSION 5: ADDITIVE DEVELOPMENTS

IMPROVEMENT OF DIESEL FUEL PROPERTIES BY ADDITIVES

Bharati Chheda and Rajiv Banavali

In recent years, environmental regulations have had a significant impact on the formulation of Diesel fuel. The introduction of new fuel specifications with lower aromatics and sulfur content and higher cetane number, coupled with the rapid changes in engine design, have created the need to address several fuel properties to ensure proper performance. Today, the diesel fuel is increasingly produced by catalytic cracking of heavy crude oil to meet the demand. Catalytically cracked distillate fuels present different challenges compared to the straight-run distillate fuels because of the differences in the chemical composition. Fuel additives can address the performance issues of today and future fuels. In this paper, we will focus on various fuel performance enhancement needs such as long term and thermal stability, detergency, cetane number, and lubricity. We will discuss mechanisms by which the fuels and additives interact to promote the performance enhancement.

EFFECT OF NEW ADDITIVE TOWARDS MITIGATING THE ADVERSE EFFECT OF CETANE IMPROVER ON DIESEL FUEL THERMAL STABILITY.

J. Andrew Waynick and Matthew E. Gande

The potentially adverse effect of the cetane improver 2-ethylhexyl nitrate on No. 2 diesel fuel thermal stability, as measured by ASTM D6468, has been known for years. A relatively new class of additives has been evaluated by ASTM D6468 for its ability to significantly reduce that adverse effect. Several different members of this class of additives have been evaluated and their performance compared against each other in a No. 2 diesel fuel that is sensitive to the adverse effect of cetane improver.

SESSION 6: DISTRIBUTION

A STUDY OF ADDITIVATED LOW SULPHUR DIESEL DURING TRANSFER THROUGH SHARED PRODUCT PIPELINES FROM REFINERY TO THE FUEL CONSUMER

Ariela Rave and Josefa Ben-Asher

The introduction of low sulfur diesel fuel into Israeli market required an extensive additivation of the product. Suitable additives were added at the Refinery to improve Lubricity and Cold Filter Plugging Point properties of the fuel. This switch created a host of handling uncertainties. For instance:

-The lubricity additive is a surface-active chemical. The question was whether diesel that left Refinery on- spec would reach the fuel consumer as such.

-For terminals receiving fuel by a shared product pipeline, there is currently no reliable way to detect the interface between low- sulfur and high sulfur products in time to swing valves and avoid front-end or back-end contamination. We wanted to know whether with the existent technology the low sulfur diesel that leaves the producer on-spec still complies with the requirements at the final destination.

-The low sulfur diesel is a product of intensive hydrogenation and its conductivity is close to zero at the point of production. A fuel with poor conductivity may build up a static charge that if discharged as a spark. In a combustible air fuel mixture, an explosion or fire may occur. Our aim was to determine whether a danger of build up of static charges, at the truck loading facilities, could be expected.

Samples were taken from the Refinery tanks and analyzed for compliance with specification requirements. The diesel route was followed through the terminals and sampled at each stop. The properties that were studied: Lubricity as per ISO-12156-1, Sulfur Content as per ASTM D 4294, Conductivity as per ASTM D 2624 and CFPP as per IP 309. No significant change was found in Sulfur Content and Lubricity of fuels that were transported through multi-product pipelines to the end user. We found though fluctuating results of CFPP property. The conductivity rose as the fuel progressed down stream and therefore no danger was anticipated at the end user facilities from build up of a static charge.

THE PRACTICAL USE OF ISPG ABOVE GROUND TANK MODULE IN JAPAN

Jun Shigeta, Tsuyoshi Yokoyama, Takao Hara, Hiroaki Maruyama

Since 1998, Japan National Oil Corporation (JNOC) has developed Crude Oil Sludge Prediction System for above ground tank as the experimental center of International Sludge Project Group (ISPG). The method of EQPS (EBV Quality Prediction System for long-term storage of oil products) was applied to this prediction system and the system had been completed in June 2001. This prediction is the risk analysis using decision tree with many function groups and original variables on the fall-out phenomena. And the prediction result is given for a recommendation of 27 levels. Although the sludge prediction is not clarified at present, this system will be expected to back up the operations and maintenance at storage sites. Therefore JNOC has selected some original variables as minimum input data and started to apply this system to six crude oil storage sites since April 2002. This paper deals with the practical use of the crude sludge prediction system and the sensitivity analysis of the selected variables for the improvement of this system.

SESSION 7: LOW TEMPERATURE OPERATION

OPERATION OF AIRCRAFT FUEL SYSTEMS AT LOW TEMPERATURES

Steven Zabarnick, Mark Laber, Jamie Ervin, and Rajee Assudani

Commercial jet aircraft are currently limited to operating at measured fuel temperatures that are greater than 3°C above the fuel specification freeze point. The recent opening of long duration, polar routes results in fuel tanks being subjected to lower temperatures for longer periods of time. When the measured in-tank fuel temperature approaches these low temperature limits, pilots are forced to modify flight path, altitude, and/or airspeed to raise these temperatures. Many jet fuels have freeze points that are significantly lower in temperature than the fuel specification.

Airline companies would like to change the low temperature operational limit to greater than 3°C above the measured freeze point of their particular fuel. Such a change could minimize unnecessary flight path, altitude, and/or airspeed alterations. We have undertaken the study of the effect of operating fuel systems at these low temperatures. We have designed and built an aircraft wing tank simulator that can be subjected to low temperatures inside an environmental chamber. The simulator employs actual B747 fuel boost pump and flapper valves. The fuel flow rates, temperature profiles, pump current, and pressures are measured as a function of temperature. We have also performed a series of laboratory studies to better characterize fuels at these low temperatures. These include differential scanning calorimetry; low temperature scanning Brookfield viscometry; and freeze, cloud, and pour points. In particular, the change in viscosity at these low temperatures is especially significant for operation of the fuel system. We have also studied the mixing of two fuels with different freeze points. Such fuel intermingling occurs routinely upon aircraft refuelling, and can be problematic if the freeze point of the resulting fuel mixture is higher than either of the two original fuels. In addition, we have undertaken a computational fluid dynamics study of our wing tank simulator to allow prediction of fuel temperatures in real fuel systems.

DEVELOPMENT OF LOW TEMPERATURE ADDITIVES FOR USE IN JET FUEL

Cynthia A. Obringer, Jamie S. Ervin, Stephen Zabarnick, Theodore F. Williams, Marlin D. Vangsness, Linda M. Shafer, Gordon L. Dieterle and Kenneth E. Binns

Due to the low temperatures encountered at high altitudes air vehicles are currently limited to about 40,000 feet. High-altitude military aircraft currently use JPTS, an expensive specialty fuel. JPTS is a kerosene based fuel similar to JP-8 but with increased thermal stability and decreased freeze point. A thermal stability additive, +100, has been developed that when added to JP-8 results in meeting or exceeding the thermal stability properties of JPTS ("JP-8+100: Development of a Thermally Stable Jet Fuel," S. P. Heneghan, S. Zabarnick, D. R. Ballal and W. E. Harrison, *Journal of Energy Resource Technology*, vol. 118, pp. 170-179, October 1996). A program is currently underway to develop a low temperature additive that when added to JP-8 will result in low temperature properties that meet or exceed those of JPTS. Currently JP-8, the standard military jet fuel, is limited to temperatures above –47°C. Cloud point depressant and wax crystal modifying additives that are capable of improving the low temperature behaviour of jet fuel by approximately 10°C have been developed. The low temperature behaviour of these additives has been analyzed for low temperature performance. Simple laboratory scale tests including low temperature viscometry and microscopy and differential scanning calorimetry have been used as well as larger scale simulators. This paper will report on the results of this effort.

LOW TEMPERATURE IMPROVEMENT OF BIOFUELS

David R. Forester, Robert Barbour , David Price, and Nancy Strete

Bio-fuels derived from seed oils, such as rapeseed or soybeans, have been available on a limited basis within North America and Europe since the early 1990's. A number of technical problems with the use of biodiesel have been discussed in the literature. Perhaps the most significant technical issue that additive treatment could address with the use of biodiesel is the upgrading of Cold Filter Plugging Performance (CFPP) in `B100' and other high biodiesel content blends. While the projected market in the US is still being developed, a total annual European demand for CFPP additive of at least 5,000 MT's is estimated by 2010. Numerous additives have been reported in the literature which allegedly reduces CFPP. Additives such as styrene-maleic anhydride copolymers, polymethacrylates (PMA), and ethylene-vinyl acetate (EVA) copolymers have been claimed. Previous work at Lubrizol confirmed that EVA chemistries alone are ineffective at producing substantial reductions to CFPP in B100's. A previous LZ product based on MSC ester chemistry was shown to reduce CFPP to –20^{o}C at a 0.75% treat rate into European biodiesels. This paper will present the application of a variety of Lubrizol chemistries, including synthesized polymers, as CFPP and pour point reduction additives. Products for B100 based on soy methyl ester (SME) and B20 blends of SME with diesel have been commercialized. Also, more cost-effective synthesized polymers for B100 based on rapeseed methyl ester (RME) for the European market have been prepared for evaluation by potential customers.

SESSION 8: FUEL STABILITY

STABILITY CHARACTERISTICS OF SELECTED BIODIESEL FUELS AND B20 BLENDS

Steven R. Westbrook and Leo L. Stavinoha

Biodiesel fuels are known to be especially susceptible to oxidative degradation. Thermal stability of diesel fuels is also of growing concern to both equipment manufacturers and end-users. This paper presents the results of a study of the oxidative and thermal stability characteristics of several biodiesel fuels made from various raw materials. Selected antioxidant additives were also evaluated for their efficacy in these fuels. Several B20 blends were also tested with and without antioxidant. The fuels were aged using modified versions of ASTM method D2274, Oxidation Stability of Distillate Fuel Oil (Accelerated Method) and ASTM D6468, High Temperature Stability of Distillate Fuels. The aged fuels were tested for total acid number, particulates, steam jet gum, and viscosity. Results were also compared to results for fuels stored at 43°C, ASTM D4625.

AN INTERPRETATION OF A RECENT SINGLE TUBE FLOWING REACTOR SYSTEM (ECAT) STUDY OF A JP-8 THROUGH THE LENS OF THE ZABARNICK-HENAGHAN AND ETIO HYPOTHESIS

Bruce D. Beaver and Michel G. Fedak

We use two extent mechanistic hypotheses to explain the previously published behavior of a JP-8 under +225 stressing in a single tube flowing (ECAT) system. The Zabarnick-Henaghan (Z-H) hypothesis accounts for the observed oxidative deposit formation under the +225 conditions of total oxygen consumption. The presence of 256 ppm of the Betz +100 additive package (8Q462, composed of MDA, BHT and a dispersant/detergent) is found to decrease oxidative deposit by greater than 60%. The presence of 200 ppm of triphenylphosphine (TPP) was found to decrease oxidative deposit by approximately 50%, both in the presence and absence of the Betz +100 additive package. Presumably, the Betz +100 package is not very effective in the presence of TPP. It is proposed that this result is due to two effects: First, oxygen scavenging by TPP, via operation of a non-radical ETIO mechanism, decreases the oxidative degradation of the fuels indigenous antioxidants. Thus, less deposit is generated in the presence of TPP. Second, TPP initiates, via a radical ETIO mechanism, an alkoxyl radical flux that promotes the oxidative degradation of the dispersant/detergent additives. In this manner the observed minimal effect of dispersants/detergents in the presence of TPP in one JP-8 can be explained.

REMOVAL OF DRAG REDUCER ADDITIVE FROM PETROLEUM FUELS, PART 1: GASOLINE AND THE RHEOLOGICAL BEHAVIOR CATEGORY

J. Andrew Waynick

Twenty-seven carbonaceous solids were evaluated for their ability to remove, via adsorption, drag reducer additive (DRA) from an unleaded, base gasoline. Three different contact methods of differing efficiencies were used for mixing carbon with DRA-containing fuel. The effect of pre-heating the carbons prior to evaluation was determined. Behavior of the carbons during contact with the DRA-containing gasoline was noted and correlated to adsorption efficacy. Results indicated that carbon adsorption efficacy varied widely, with some carbons removing essentially no DRA polymer from the base gasoline, and with others removing more than half the polymer. Maximum observed adsorption capacity was nearly 0.2%. Carbon performance was also strongly dependent on the contact method used, with adsorption typically improving as carbon/fuel mixing severity increased. The dependency of carbon adsorption performance on contact method was explained by using a newly defined parameter, the Rheological Behavior Category (RBC). RBC values of 1,2, or 3 were assigned to each carbon, depending on the amount of clumping behavior observed during the mixing of the carbon with the DRA-containing fuel. By observing certain correlations between a carbon's RBC and its ability to remove DRA polymer, a viable adsorption model was developed. This paper, the first of a series, presents some background information pertaining to the development and commercial use of DRA in the petroleum industry, a description of the evaluation methodology used, a discussion of results, and conclusions that derive from those results.

SESSION 9: TEST METHODS

EXPERIENCES WITH NEW TEST METHOD TO ASSESS GAS OIL IGNITION QUALITY

Jacco D. Woldendorp

The current established test method to measure diesel ignition quality is ASTM D 613. This engine test method, however, has several drawbacks: it's awkward, needs experienced skilled operators, and is not readily available. Therefore the industry has welcomed a new technique to measure the ignition quality of diesel. This technique, developed by SouthWest Research Institute (SWRI), is a combustion based analytical instrument, in which the ignition delay is measured in a constant-volume combustion chamber at diesel auto-ignition conditions, i.e. high temperature (ca. 550 °C) and high pressure (ca. 22 bars). This technology was further developed commercially for laboratory and refinery use by Advanced Engine Technology Ltd (AET) in Ontario, Canada: the Ignition Quality Tester (IQT™). The IQT™ uses a correlation model that translates the measured ID into the Derived Cetane Number (DCN) which itself relates (but is not equivalent) to the engine cetane number. The methodology has been accepted by the Institute of Petroleum (IP 498/03) and ASTM. The main oil companies (i.e. Shell, BP, Exxon) support this new technology. They have spent significant effort making this technology accepted for specification purposes: as alternative to the engine test method for the short term and as established test method for the longer term. It is envisaged that the engine test method will become obsolete. Also the empirical estimation of cetane number by cetane indices is becoming less reliable and usable due to the move to much more stringent diesel fuel specifications, featuring high cetane number specifications rather than cetane indices, the drive to use cetane ignition improvers cost effectively to meet these new high cetane number specifications, and the appearance of non-traditional components in the diesel pool (i.e. SMDS gas oil, biodiesel). Shell Global Solutions is using the IQT™ since April 2000 and is playing an active role in its test method standardization process. This paper shares our experience built so far. The following issues will be discussed: implementation of equipment, maintenance, service support, international test method standardization and specification, examples of applications, and future developments.

A NEW STORAGE STABILITY TEST METHODOLOGY FOR DIESEL FUEL

Dennis Hardy and Seetar Pande

Most standardized accelerated storage stability test methods for diesel fuel employ temperature regimes between 40 and 100 degrees C and headspace composition ranging from air to pure oxygen at pressures between atmospheric and 100 psi gauge. Test times range from 16 hours up to 18 weeks. Clearly the most realistic tests at lower temperatures and pressures are excessively long for the purpose of predicting future stability. At 43 degrees C the accepted time to estimate ambient storage at 1 year would be a test time of 13 weeks (equal to about 90 days or 2200 hours). Employing a rough Arrhenius logic to the time and temperature trade-off at atmospheric air pressure would indicate that at 90 degrees C a test time of about 70 hours or 3 days would equate to ambient conditions. At 100 degrees C we would expect a 35 hour test time to equate to ambient conditions. At these higher temperatures an attempt is usually made to shorten the test time to less than 24 hours by sparging with air or oxygen. However, the only successful method of shortening the test time has been by pressurizing with air or oxygen. A test such as the D5304 test at 100 psi oxygen for 16 hours at 90 degrees C will adequately simulate several years of storage at ambient conditions. Higher temperatures can be used (up to 150 degrees C) in an effort to shorten the test time to as short as 1 hour (such as D6468). This paper reports on some work done at 150 degrees C and ambient air at atmospheric pressure conditions. The initial work employed gravimetric determinations of filtered samples and showed good correlation to D5304 conditions (and thus to ambient conditions). It appears that neither sparging nor pressurization with air or oxygen is needed at these higher temperatures. The increased rate of gas dissolution at the higher temperatures (due to decreased viscosity of the liquid) may play an important role in simplifying the test methodology at these higher temperatures. Details of the work done to date will demonstrate the correlations of the 150 degree C test. At that temperature it is possible to get realistic and accurate gravimetric data in several hours. This work forms the basis for the development of greatly improved standard test methods for both commercial use (predicting up to 6 months of stability) and for military use (predicting up to 3 years of stability).

DEVELOPMENT OF A RAPID, ON-SITE METHOD FOR THE DETERMINATION OF COPPER IN JET FUELS

Robert E. Morris, Greg E. Collins, Qin Lu, Jing-Fong Wei, Pamela M. Serino and Yan Guo

Many petroleum products, including refined fuels, acquire low levels of various metals upon exposure to alloy surfaces during storage and handling. Copper, in particular, has been implicated as an autoxidation catalyst that can severely degrade the thermal stability of jet fuels during use. While the amount of copper necessary to do this varies with different fuels, it is generally agreed that levels above 20 parts per billion (16 μg/L) should be avoided. The determination of copper in fuel to that level is nontrivial, with graphite furnace-atomic absorption spectroscopy being the only currently reliable method available. To meet the need for the rapid, on-site detection of ppb levels of copper in jet fuel, we have investigated several colorimetric indicators for use in a spectrophotometric method. Two spirobenzopyran dyes, quinolinospiropyranindoline (QSP) and nitrospiropyranindoline (NQSP) were examined, since they respond sensitively to various metal ions in fuel, including copper, nickel and zinc. Selectivity for copper was achieved through the application of principal component analysis, a technique that also provided a means for simultaneously determining zinc and nickel levels in jet fuel. However, the need to obtain a copper-free baseline sample of the test fuel and the interferences introduced by metal deactivating additives, limited the precision of NQSP. Bathocuproine (BCP), a well-known reagent for the selective determination of Cu(I), and for total copper, when combined with a suitable reducing agent, can be introduced directly into a jet fuel sample and colorimetrically measured using a portable fiber optic spectrometer. In combination with a reducing agent (ascorbic acid), and a solubilizing agent (ethanol), BCP was successfully used to determine total copper content in jet fuels from a number of different sources and handling histories. Moreover, the BCP method does not have the limitations of NQSP. The detection limits, based on a signal/noise ratio of 3:1, were 7.8 ppb (6.2 μg/l) with a benchtop dual beam spectrophotometer and 9.4 ppb (7.5 μg/l) with a portable fiber optic spectrometer.

SESSION 10: SYNTHETIC FUELS

SYNTHETIC JET FUELS AND THEIR ROLE IN THE FUTURE

Joanna M Bauldreay, Richard J Heins, and Johanne Smith

Performance and safety have always guided the setting and improving of aviation fuel specifications. Compared with road fuels, jet fuel requires far more tests to ensure it meets all quality requirements and is fit for purpose. The major specifications are also quite explicit in what may be used as a feedstock for aviation fuels. Not surprisingly, the advent of fuels produced by significantly different routes and from different feedstocks concerns the aviation industry. Synthetic (as derived from a Fischer-Tropsch process) kerosines are the latest class of novel materials to be considered as potential jet fuel components. Sasol kerosine is used under very tightly controlled conditions when produced at one location in South Africa, and is the only synthetic component approved for jet fuel blends. Other companies are producing other synthetic kerosines, by a variety of process routes. The Shell Middle Distillate Synthesis process starts with natural gas. One-by-one approvals will be too costly for the industry to bear yet such components must become part of the jet fuel pool if there is to be enough fuel to meet projected demands for flight. This paper will provide reasons to welcome such fuels in the aviation industry. Performance and other data will show how synthetic fuels have many properties that make them superior to traditional and less regulated crude oil derived kerosines. The paper will also indicate how a truly performance-based requirement may allow all aviation fuels to be judged by the same compositional criteria, irrespective of their processing history.

STABILITY AND FUEL/ADDITIVE COMPATIBILITY CONSIDERATIONS OF SASOL FULLY SYNTHETIC JET FUEL

Dr. Clifford A. Moses, and George R. Wilson III, and Piet 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. Among the concerns and issues with synthetic jet fuels are their oxidative and storage stability and compatibility with common fuel additives and conventional fuels. This paper demonstrates that Sasol synthetic kerosene streams have excellent stability under both accelerated storage and thermal oxidative conditions. Common fuel additives are soluble at the required concentrations and are effective in their function. When co-mingled with conventional jet fuels, no problems have occurred with separation or formation of particulates under either hot or cold storage conditions.

ELASTOMER COMPATIBILITY OF SASOL FULLY SYNTHETIC JET FUELS

Dr. Clifford A. Moses, and George R. Wilson III, and Piet 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. One of the major concerns with synthetic jet fuel from gas-to-liquid processes is the total lack of aromatic hydrocarbons that are considered necessary for inducing swell in certain elastomeric seals to prevent fuel leaks in aircraft fuel systems and ground handling equipment. However, since Sasol uses its Fischer-Tropsch processes to produce gasoline and diesel fuel as well as specialty liquids, product streams have been identified for use as kerosene that do contain aromatics. This paper demonstrates that the synthetic aromatics in Sasol's synthetic kerosene streams are single-ring aromatics in the jet-fuel boiling range that are compatible with common elastomeric compounds and will not cause problems with seals in aircraft fuel systems or ground handling equipment.

SESSION 11: MICROBIOLOGY

LATEST INDUSTRY INITIATIVES IN DEVELOPMENT OF STANDARD SPECIFICATIONS AND PROCEDURES FOR CONTROL OF MICROBIAL CONTAMINATION IN FUELS

Graham C. Hill and Edward C. Hill

At the 7th IASH 2000 Conference, Passman provided attendees with an update on guideline documents addressing the investigation and control of microbiological contamination of fuels. The subject has attracted considerable industry interest since then, with recent or imminent publication of four further industry reference documents including;

- *IATA Guidance Material on Microbiological Contamination in Aircraft Fuel Tanks, November 2002*
- ASTM Manual 47: *Fuel and Fuel System Microbiology - Fundamentals, Diagnosis and Contamination Control, 2003*
- *"Microbes in the Marine Industry", Institute of Marine Engineering, Science & Technology, 2003*
- *IP Guidelines on Microbial Contamination in Fuels* (revision document, in press at time of writing)

New standard test methods have also been published and approvals granted to a number of commercially available field tests. Numerous implications arise both for fuel users, distributors and suppliers. For example, the IATA document defines 3 increasing contamination levels for aircraft fuel tank drain samples, measurable using simple on-site tests. The issue of whether there should be a microbial specification for fuel then arises. The new ASTM Manual 47 and the latest IP Guidelines lay down comprehensive guidance for investigation of microbial contamination in fuel systems. These documents will set the benchmark for industry in terms of what they can be expected to do to minimize the risk of microbiologically related operational problems. There is evidence that such problems are on the increase. This paper puts the risks of microbial contamination in fuel, and the associated operational problems, into perspective. It considers the suitability of current industry guidance on fuel handling (e.g. JIG Guidelines for Aviation Fuel Quality Control) in relation to microbiological contamination issues. It also discusses the latest microbiological documentation and the implications for fuel handling practice, filtration, maintenance and quality control.

NON-CONVENTIONAL METHODS FOR ESTIMATING FUEL SYSTEM BIOBURDENS RAPIDLY

Frederick J. Passman, Larry Loomis, Jack Sloyer

Three alternative, non-conventional test methods are evaluated for their ability to detect and quantify bioburdens in fuel and bottom-water samples. Two of the parameters, catalase activity and adenosine triphosphate (ATP) concentration have been used previously. This is the first report of the use of fluorescence polarization (FP) technology for fuel and fuel-associated water testing. In this investigation, each parameter is assessed for repeatability and reproducibility. Covariance amongst the three non-conventional test method data is reported. Covariance between each of the non-conventional parameters and each of a variety of conventional parameters (viable bacteria and fungi enumeration data, fuel and bottom water chemistry) is also reported. Although each test method has limitations, the new methods reported in this paper may contribute significantly to fuel system microbial contamination condition monitoring and biodeterioration root cause analysis efforts.

FIELD USE OF TETRAKISHHYDROXYMETHYL PHOSPHONIUM SULFATE IN NORTH AFRICA

Ed English

In 2000 a tetrakishydroxymethyl phosphonium sulfate (THPS) biocide was introduced into an oil field in North Africa. This particular field had been using various formulations of aldehyde based and quaternary amine based biocides for several decades while continuing to experience operational challenges. In 2002, after using the THPS based biocide for approximately 18 months, the challenges associated with daily operation improved. The user attributed the improved performance to the use of THPS based biocide. This paper will discuss the biocide, its application and field performance during and since the initial field trials of the material

SESSION 12: FUNDAMENTAL SCIENCE & MODELLING II

THE APPLICATION OF NUMERICAL PATTERN RECOGNITION TO CORRELATE FUEL COMPOSITION WITH PERFORMANCE AND STABILITY

Robert E. Morris, Kevin J. Johnson and Susan L. Rose-Pehrsson

Recent advances in the field of chemometrics have provided us with an opportunity to determine if it is possible to extend numerical multivariate pattern recognition techniques beyond simple fuel characterization, to the identification of important compositional features that are related to fuel quality. This can include unique combinations of normally benign constituents that exert an impact on fuel stability. Fuels are ideal candidates for chemometric analysis, since we are often concerned with minute features within a complex compositional matrix. Two potential benefits of this approach are the development of diagnostic and predictive models that can relate fuel composition to quality. We have begun our investigation with studies of gas chromatography-mass spectrometry (GC-MS) data from fuels that have undergone various levels of thermally induced autoxidation. Analysis of variance (ANOVA) GC-MS feature selection was developed to locate features that changed from sample to sample, thus allowing for a quick evaluation of how fuel composition was altered during stress. In this manner, it was found that evaporative losses, rather than fuel degradation dominated the chemical variations produced in naval distillate fuels (NATO F-76) during oven stress at 60°C. Thermal stress in a closed low-pressure reactor (LPR) eliminated evaporative losses, and the chemical changes were readily observed and modeled. A progressive change in composition during both oven and LPR stress was revealed from multi-way principal component analysis. Decomposition of windowed regions of the GCMS data by parallel factor analysis provided a means of extracting the mass spectra of individual fuel constituents that changed during stress, identified from the ANOVA feature selection. This illustrates the potential diagnostic capability of multi-way chemometric analysis of GC-MS data.

THE ROLE OF ASPHALTENE FRACTION ON THE FORMATION OF W/O-TYPE EMULSION DURING LONG-TERM STOCKPILING OF CRUDE OIL

Takao Hara, Hiroaki Maruyama, Yoshio Watanabe, Shin-ichi Kaida, Kiyomasa Shinbori,
Yoshihiko Kon, Takeshi Takasago, Yoshitaka Sueyasu and Hajime Okano

Organic sludge deposited during long-term stockpiling of crude oil reserved by Japan National Oil Corporation (JNOC) is composed of n-paraffins of substantially high carbon numbers existing in the W/O-type oil-water emulsion. 7 kinds of crude oil delivered from Middle East and reserved by JNOC (API degree: 36.6～28.4) were mixed with water (50/50vol%) under the certain shear rate to form W/O emulsion in the whole phase. The stability of the emulsion was evaluated by two parameters of ζ-potential of the oil-water interface and 95% volume average diameter of water drops. Because the asphaltene fraction plays a crucial role in the formation of the emulsion, a numerical analysis was applied to estimate the two stability parameters by the chemical and structural properties of the asphaltene isolated from the crude oil. The parameters (ζ-potential and average diameter of water drop) could be successfully expressed by the functions composed of 4 and 3 variables, respectively. The chemical structure of asphaltene, which might be responsible for the formation of the emulsion, was discussed. In the course of stockpiling operation under the control of JNOC, some highly stable W/O emulsions were found after the transferring process of crude oil from one storage tank to another for the safety inspection of the tank, including so-called crude oil washing (COW) procedure. The analysis of the asphaltene isolated from such emulsion could confirm the reliability of the numerical treatment mentioned above.

PREDICTING THE THERMAL STABILITY OF JET FUEL: ANALYTICAL TECHNIQUES TOWARD MODEL VALIDATION

Lori M.T. Balster, Steven Zabarnick, Richard C. Striebich and Matthew DeWitt

This paper presents the development of advanced analytical procedures for measuring polars, reactive sulfur species, and hydroperoxides to be used as input for development of a chemical kinetic model capable of predicting jet fuel oxidation and deposition behavior. An HPLC-based method is presented which accurately measures trace level polar species (i.e., naturally occurring phenols, or other polar molecules containing oxygen, nitrogen and/or sulfur), which have been shown to slow oxidation and have a detrimental effect on thermal stability. These polar compounds will be quantified and measured as a class rather than speciated as individual compounds. Closely related to this polars technique is a relatively new method to measure and quantify reactive sulfur-containing components. This technique classifies the sulfur compounds by selective oxidation at low temperatures with hydrogen peroxide and iodine. Finally, new ways of determining organic hydroperoxide content by reaction with triphenylphosphine shows promise in accurately measuring the reactive hydroperoxides. The resulting data obtained from these non-routine analyses will be used to develop a pseudo-detailed mechanism for jet fuel oxidation and deposition. These mechanisms require the group-type determinations of important reactants such as polar component concentrations, reactive sulfur levels, and hydroperoxide content for the prediction of oxidation and deposition in hydrocarbon fuel systems.

SESSION 13: FUEL CONTAMINANTS

EFFECT OF RED-DYE CONTAMINATION ON THE FOULING RATES OF AIRCRAFT FUEL NOZZLES

Dr. Clifford A. Moses, and George R. Wilson III, and H. Stewart Byrnes

An experimental study of the effect of diesel-fuel red dye contamination on the thermal stability of jet fuel has been undertaken by the FAA with multiple sponsorship including the US Defense Energy Support Center, the Airline Transport Association, the engine and airframe manufacturers, and the American Petroleum Institute. The program has two objectives:

- to quantify the effect of red dye contamination on fuel thermal stability
- to identify and validate a methodology for evaluating thermal stability issues

The effort to meet the first objective consisted of two phases: 1) a screening effort to identify and select a test fuel that had a thermal stability that was sensitive to red dye, and 2) a series of fuel-system hardware fouling tests to quantify the effect of red dye on fouling life. This paper reviews the results of the fouling tests on nine different types of fuel nozzles representing large and small engines from commercial and military aircraft. It was found that 0.55 mg/L of red dye can lower the JFTOT breakpoint by 10 to 15C and cause as much as a four-fold increase in the fouling rate of fuel nozzles.

EFFECT OF COPPER CONTAMINATION ON THE FOULING RATES OF AIRCRAFT FUEL NOZZLES

Dr. Clifford A. Moses, and Richard A Kamin

Tests have been conducted to evaluate the effect of copper contamination in JP-5 fuel on the fouling rate of fuel nozzles the engine of a modern Navy aircraft. The tests were conducted in a thermal environment that simulates actual engine installation at the beginning of idle descent. This is the flight condition with the highest fuel-wetted wall temperatures inside the nozzle and consequently the highest fouling rates. The results were consistent with the fouling rates determined on earlier tests of this nozzle with several other jet fuels of different thermal stability, i.e., JFTOT breakpoint temperature. The fouling rates at fuel temperatures less than 360F followed an exponential correlation with fuel temperature. However, at a fuel temperature of 360F, the fouling rate was about 5.5 times higher than would be predicted from the correlation at the lower temperatures. It is speculated that at fuel temperatures less than 310F, the effect of the copper contamination on fouling rate would have been negligible.

AIRCRAFT HYDRAULIC OIL IN AVIATION TURBINE FUEL – ALLOWABLE LEVELS

Stanford Seto

The airlines request permission to do a non-revenue flight to return an aircraft that has had a leak of hydraulic oil into the fuel tanks to a maintenance base. Small scale testing was done to assess the effects of aircraft hydraulic oil (contains phosphorous, potassium and sodium) contamination of commercial aviation turbine fuel (Jet A, Jet A-1) on the properties of fuel system elastomeric materials and 440°C stainless steel, which is used in the construction of the fuel nozzle metering valves and tip orifices, and the fuel thermal stability property. The contaminated fuel was burned in a one atmosphere combustion chamber and the hot gas stream there from was passed over samples of coated and uncoated combustor and turbine hot section flow path materials to determine the erosion and corrosion effects on the coatings and materials. The concentration of hydraulic fluid in the fuel was set at 0.50 and 2.0% by volume. The hydraulic fluid was weathered to its maximum acid level for the elastomeric soaking tests and for the assessment of fuel thermal stability change, but due to the quantities of hydraulic oil used, not weathered for the combustion tests. The elastomers, Nitrile, Fluorosilicone and Fluorocarbon, all passed the soaking tests at 60°C, but the Fluorosilicone disintegrated when soaked at 200°C. The 440°C stainless steel exhibited no effects when soaked at temperature. The combustion tests showed that the coated material samples were less vulnerable to the hot gas exposure, whereas the uncoated samples exhibited greater corrosion and erosion rates, with one exception. Metallurgical analysis of the samples is reported in an accompanying report.

SEPARATION OF WATER FROM W/O-TYPE EMULSION FORMED DURING LONG-TERM STOCKPILING OF CRUDE OIL

Takeshi Takasago, Kiyomasa Shinbori, Yoshihiko Kon, Yoshitaka Sueyasu, Hajime Okano, Hiroaki Maruyama, Yoshio Watanabe, Shin-ichi Kaida and Takao Hara

In the course of the strategic stockpiling operation of crude oil under the control of Japan National Oil Corporation (JNOC), some viscous W/O-type oil-water emulsion has been found to be deposited on the bottom of the above-ground floating-roof storage tank. Such emulsion could be converted into so-called hard sludge as water content of the emulsion increases. In the present paper, the possibility of oil-water separation from W/O emulsion was studied by adding a combination of demulsifiers in a laboratory scale. 7 kinds of crude oil delivered from Middle East and reserved by JNOC (API degree: 36.6～28.4) were mixed with water (50/50vol%) under the certain shear rate to form W/O emulsion in the whole phase. The stability of the emulsion was evaluated by a newly proposed J value as a function composed of two parameters, namely, ζ-potential of the oil-water interface and 95% volume average diameter of water drops. Among 15 kinds of demulsifier and a certain combination of them, most effective and efficient combination for oil-water separation could be chosen along with J value. The findings were applied to an actual W/O emulsion derived from oil storage bases and a practical application for demulsifier was demonstrated.

SESSION 14: FUEL STABILITY

THE IMPACT OF COPPER-CONTAMINATED JP-5 ON THERMAL MANAGEMENT SYSTEMS OF ADVANCED AIRCRAFT

John E. Colbert and Clarence J. Nowack

Vital components of advanced aircraft require cooling during flight, and the fuel is an essential part of the thermal management scheme. Bulk fuel temperatures are expected to reach 150°C (302°F) or higher, and many studies have shown that the fuel would be at its thermal limit. In order to prevent an over-temperature condition, the fuel is recirculated back from the engine to the airframe as a means of keeping the temperature below the maximum limit. This problem may be further exacerbated when these aircraft operate with copper-contaminated fuel, a problem that is unique to the Navy due to their use of copper-alloy plumbing in the shipboard fuel distribution systems. The purpose of this experimental study is to determine the thermal deposition potential of a copper-contaminated fuel (versus an uncontaminated fuel) under hot recirculation conditions over a bulk fuel temperature range representative of advanced aircraft fuel systems. Two different fuels were evaluated in two laboratory test devices, one laminar flow and the other turbulent, over the temperature range from 135 to 177°C (275 to 350°F) under single pass and 5X recycle conditions. The results show that a significant amount of deposits are produced at 177°C (350°F) under *single pass* conditions for the two neat fuels in both test units, and the rate is twice that when these fuels were contaminated with 250 to 300 ppb copper. For *recirculation*, both devices produce higher deposition rates for both neat and copper-contaminated fuels over the temperature range tested, with copper producing nine times more deposits at 177°C (350°F) as compared to the neat fuel. Moreover, the presence of copper yields more deposits that are larger in size as well as higher existent gums, per pass and after the 5th pass, as compared to the uncontaminated fuel. In addition, much of the soluble copper was depleted from the fuel after the 5th pass, and this depletion rate was higher as the temperature was increased.

THE EXAMINATION OF LIQUID-PHASE OXIDATION TO DEFINE THE IMPACT OF COPPER ON JET FUEL THERMAL STABILTIY IN ADVANCED AIRCRAFT

Robert E. Morris and Janet M. Hughes

It is anticipated that as military aircraft technologies are advanced, the thermal demands placed on the fuel will also increase. Thus, it is necessary to revisit the issue of fuel thermal stability, in light of these advanced engine fuel systems. The impact of copper contamination will continue to be an issue for the US Navy, as long as copper-bearing alloys are present in shipboard fuel handling systems. In this study, we have focused on three aspects of JP-5 copper contamination that may have an impact of fuel suitability in advanced aircraft. 1) The maximum impact of high levels of dissolved copper on fuel oxidation over a relevant temperature range; 2) the relevance of using a copper chelant vs exposing the fuel to copper metal as a means of introducing copper for laboratory testing; and 3) the extent to which copper entrained in insoluble precipitates formed from copper-bearing fuels can act as a catalyst for further degradation in a recirculating fuel system. Examination of liquid-phase oxidation by analyses of oxygen consumption and hydroperoxide formation rates were used to define the impact of copper to accelerate fuel oxidation in a flow system as a function of both temperature and copper concentration. Thus, the oxidation regime of a fuel can be represented graphically in a plot that expresses the impact of temperature and copper concentration on liquid-phase oxidation for any particular fuel. It was also found that if the copper residence time was relatively short, i.e., days or weeks, as opposed to months or years, that it made no appreciable difference whether copper was introduced from exposure to copper metal or from a chemical compound. It was also shown that the catalytic activity of copper entrained in fuel sediments was negligible on JP-5 oxidation at temperatures up to 150°C (302°F), in a stirred reactor with limited oxygen availability.

PEROXIDE FORMATION IN ULTRA-LOW SULPHUR DIESEL FUELS

Scott D. Schwab, Joshua J. Bennett and Thomas W. Nichols

Refiners in many regions of the world are now, or soon will be required to produce diesel fuels with greatly reduced sulfur content. Given that some naturally-occurring sulfur compounds found diesel fuels are known to decompose peroxides, there has been a concern that once these compounds are removed by hydrotreating or other means, hydroperoxides will be more likely to build up during storage and use. Excessive hydroperoxide formation in hydrotreated jet fuels caused the failure of fuel system elastomers in jet engines during the early 1960's. In this paper, we present results showing the kinetics of hydroperoxide formation at temperatures ranging from 43 to 150°C in several ultra-low diesel fuels. The temperatures and aging times required to form potentially detrimental concentrations of hydroperoxides are identified. These conditions are then compared to the conditions in several standard distillate stability tests and to the measured temperatures and approximate residence times of fuel as it circulates through a diesel engine.

SESSION 15: AND FINALLY…

STUDIES OF THE LUBRICATION CHARACTERISTIC OF JET FUELS BY THE DIFFERENCE TEST METHODS

Tao Zhiping, Guozhong Dan, Cuijun Zhang

There have many test methods to be developed to assess the lubrication properties of jet fuels, but the ASTM D 5001 method is used wildly. In China, however, there is dissimilarly test method (Standard test Method for Measurement of Lubricity of Aviation Turbine fuels by the Ring-on-block" (MHK)) that is used to measure the lubricity and Standard number is SH/T 0073. Our laboratory first bas been evaluated the lubrication properties of all kinds of jet fuels produced in P.R CHINA by ASTM D 5001a and investigated the difference and relationship of lubricity tested by two methods. Furthermore, the relationship between the wear and total acidity is discussed.

A COMPOSITIONAL INVESTIGATION BETWEEN HYDROTREATING AND LUBRICITY IN A UNIQUE SET OF MIDDLE DISTILLATE FUEL

Janet M. Hughes, George W. Mushrush and Dennis R. Hardy

The compositional changes with regard to natural lubricity components that diesel fuel undergoes during hydrotreating were investigated. Six diesel fuels from the United States, England, Israel and Spain were hydrotreated to four different levels of sulfur and aromatic content. Three different ASTM methods were used to determine the lubricity of these samples. These tests showed that the lubricity of the fuels was severely impacted by the hydrotreating process. Considering that lubricity components must be surface active species, a base extraction followed by GC analysis was developed in order to investigate the role of naturally occurring acidic species within the fuel. This chemical test correlated with the ASTM tests. Additionally, GC/MS was employed to determine the major classes of compounds that are responsible for a fuel's inherent lubricity. A third aspect of this work was investigating the impact of aging on fuel lubricity. The samples were aged at ambient conditions for two years as well as undergoing accelerated aging experiments. There appears to be a fuel dependent relationship between aging and compositional changes that affords a fuel its lubricity.

RESIDUAL FUEL OIL STABILITY REVISITED

Frans G. A. van den Berg and Jacco D. Woldendorp

Precipitation of asphaltenes or other solids/sludgy materials continues to be a problem in the transportation and storage of Residual Fuel Oils (RFO). Several in-house methods for assessing RFO stability and/or stability reserve exist, but unfortunately there is as yet no generally accepted method available to the industry. ASTM Subcommittee 14 has formed a study group to evaluate currently existing techniques. This contribution will discuss potential causes of deposit formation in the RFO chain (manufacture, storage, distribution and final application), illustrated with recent practical experience. The Shell methods for determination of stability (P value) and compatibility (Po/FRmax) will be discussed and compared with several other available techniques. The latest version of the Shell Automated Stability analyser will be reviewed.

SESSION 16: POSTER SESSION

SOME THOUGHTS ON THE FUTURE SHAPE OF THE JET FUEL SPECIFICATION.
Peter Brook, Mike Farmery, Anthony Kitson-Smith, and Linda J. Rainbow.

THE LONG-TERM STORAGE STABILITY OF FATTY ACID METHYL ESTERS AND BLENDS WITH DIESEL.
Stephen W. Wall and Peter Brook.

LONG TERM SURVEY OF THERMAL STABILITY OF JET FUEL FROM A SINGLE SOURCE.
George R. Wilson, III.

JET FUEL THERMAL STABILITY AT THE REFINERY, IN THE FIELD AND IN STORAGE.
George R. Wilson, III.

PERFORMANCE RESULTS OF THPS BIOCIDE IN A NORTH AFRICAN OIL FIELD.
Ed English.

EFFECT OF CRUDE OIL CONTAINING ADDITIONAL COMPONENTS SUCH AS LOW OCTANE GASOLINE, WIDE RANGE VACUUM FRACTION, ATMOSPHERIC RESIDUE AND LOW SULPHUR CRUDE OIL ON OPERATION CONDITIONS, PETROLEUM PRODUCT YIELDS AND ENERGY COSTS FOR THEIR PRODUCTION.
G. Andonov, Sl. Ivanov, At. Ivanov, P. Kukuschkov, and D. Pehlivanov.

IDENTIFICATION OF MICROORGANISMS ISOLATED FROM UNITED STATES AIR FORCE AVIATION FUEL SUMP SAMPLES.
Michelle E. Rauch-Johnson, Harold W. Graef, Sofya M. Rozenzhak, Sharon E. Jones, Charles A. Bleckmann, Rajesh R. Naik, and Morley O. Stone.

EFFECTS OF FUEL CHARACTER ON THE PARTICULATE EMISSIONS OF A T63 ENGINE.
Matthew J. DeWitt, Edwin Corporan, Lt. Orvin Monroig, Joe Everhard and Matthew Wagner.

A SIMPLIFIED CHEMICAL TEST TO DETERMINE LUBRICITY OF MIDDLE DISTILLATE DIESEL FUEL.
Janet M. Hughes, Caitlin Williams, Dennis R. Hardy.

REPLACING GRAVIMETRY WITH BOTH PRESSURE DROP AND TIME IN MIDDLE DISTILLATE/DIESEL STORAGE STABILITY TESTS.
Christine Cary and Dennis R. Hardy.

THERMAL STABILITY OF BLENDS OF LOW TEMPERATURE FISCHER-TROPSCH PARAFFINIC KEROSINE WITH CONVENTIONAL JET FUELS.
Gregory Hemighaus and Dennis J. O'Rear.

FLEXIBLE JP-8 PROGRAM.
Pat Muzzell, Coryne Forest, and Leo Stavinoha.

EFFECT OF REFINING SEVERITY ON THE LUBRICITY OF NATO F-76 FUEL.
J. Andrew Waynick and Robert Giannini.

STABILITY AND COMPATIBILITY OF LIQUID PRODUCTS OBTAINED FROM COLD LAKE BITUMEN USING TABORR PROCESS.
Parviz Rahimi, Lee. E. Brecher, and Theo deBruijn.

A BRIEF HISTORY OF STABILITY TESTING OF MID DISTILLATE PRODUCTS AND THE POTENTIAL CONSEQUENCES OF BLENDING UPGRADED HEAVY STREAMS.
Dennis R. Hardy