

9TH INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS

**Sitges, Spain
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Abstract Summaries

SESSION 1: SYNTHETIC & ALTERNATIVE FUELS

Keynote Address:

NEW ERA, NEW TECHNOLOGIES, NEW FUEL

Martin J. Rabinowitz

Over the last one hundred years, commercial flights became reliable, comfortable, and affordable for the masses. Now we are addressing the roadblocks to making aviation environmentally friendly and safe. Fuel characteristics are keys to overcoming those roadblocks. NASA's Aero-Propulsion programs are developing new propulsion and supporting technologies that can dramatically reduce pollution, increase safety, improve economics and open new frontiers. Our radical lean-burning combustors reduce gaseous, particulate, and aerosol emissions. These exciting new technologies reduce fuel consumption and increase reliability. And, our Safety Program is developing the enabling technologies for safer on-aircraft fuel storage and passenger survivability in post crash fires. All these technologies are limited by the specified use of existing aircraft fuels. Changes in the chemical and physical nature of hydrocarbon fuels would permit the rapid advance and implementation of many of these technologies while providing more economical and robust aircraft operations. Of course, these technologies are very expensive to develop, and there is a delicate balance between the economics of fuel production and the needs of the air transportation community. Here we address some of these considerations in light of existing and future aero-propulsion technology.

IMPACTS OF SYNTHETIC JET FUEL ON THE EMISSIONS OF TURBINE ENGINE COMBUSTORS

Edwin Corporan, Matthew DeWitt, Vincent Belovich, Terry Meyer, and Amy Lynch

An investigation into the effects of a natural gas derived synthetic jet (synjet) fuel on the emissions of a turboshaft engine and a research combustor was conducted. Several blends of synjet fuel with conventional jet fuel (JP-8) were evaluated in a T63 engine and an atmospheric combustor to assess their impacts on combustor emissions and overall performance. Particulate emissions were characterized with commercially available instruments to quantify particle to quantify particle number density (PND) (particulate concentration), particle size distribution and the total particulate mass. Engine smoke numbers were measured using the standard SAE recommended practice, and gaseous emissions were quantified using a suite of gas analyzers. Test results show significant reductions in particulate mass and PND emissions for both platforms using blends of synjet fuel and JP-8 relative to operation on JP-8. As expected, due to the sulfur-free nature of the synthetic fuel,

reductions in sulfur oxides were observed with the synjet fuel and blends; however, negligible impacts on other gaseous emissions were observed. No measurable fuel flow penalties and no adverse effects on engine performance were observed with the synthetic fuel. In addition to the impacts on emissions, discussion of the physical and chemical characteristics of the blended fuels obtained using standard ASTM fuel specifications methods, and characterization of the soot exhaust particles are presented.

PROPERTIES AND CHARACTERISTICS OF SASOL FULLY SYNTHETIC JET FUEL

Dr. Clifford A. Moses, George R. Wilson III, 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 isoparaffinic 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. It has been recognized that the major fuel specifications, e.g., the British DEF STAN 91-91 and the American ASTM D 1655, are quality control specifications based on historical crude sources and refining processes. They do not define all of the properties and characteristics that a kerosene must have to be fit-for-purpose as jet fuel. For example, heat exchanger designs depend upon consistent values of thermal conductivity and specific heat, while tank gauging depends upon a relationship between density and dielectric constant. These, and many other physical properties, are not a part of any fuel specification. This paper summarizes the evaluation of 4 sample fuels produced by Sasol as representing the range of fully synthetic fuels that could be produced from coal using their Fisher-Tropsch processes. Where possible the properties are compared to surveys of current fuel.

FUEL CHEMISTRY EFFECTS ON SOOT AND PAH FORMATION IN GAS TURBINE COMBUSTION AS RELATED TO USE OF SYNTHETIC FUELS

Dr. Clifford A. Moses, Richard A Kamin, Sherry A. Williams, and Piet N. J. Roets

There is a growing interest to produce synthetic jet fuel from Fischer-Tropsch (F-T) processes to make use of energy resources other than petroleum. Most of the F-T liquids are composed of normal and iso-paraffins with near-zero aromatics. The one known exception is the Sasol fully synthetic jet fuel currently under evaluation by the British Aviation Fuels Committee for acceptance under DEF STAN 91-91. This fuel will contain aromatic hydrocarbons synthesized as part of the F-T processes. The aromatic content is expected to be less than the current average for jet fuel. It is therefore considered that all jet fuel containing F-T liquids, either as blending streams or in-total, will have less aromatics than the current jet-fuel average. Previous experience with conventional jet fuel has shown that fuels with lower aromatic content produce less soot and exhaust smoke. Tests with a T700 engine and a T700 combustor have demonstrated lower levels of flame radiation, exhaust particulates, and

polycyclic aromatic hydrocarbons (PAH) with synthetic jet fuels in line with their lower aromatic content. Surrogate fuels blended to stress different fuel hydrocarbon chemistries confirm the trends are independent of source.

B-JET PROJECT: PERFORMANCE AND EMISSION TESTING RESULTS USING BLENDS OF BIODIESEL AND JET-A IN A TURBINE ENGINE TEST STAND AND IN A FLIGHT TESTING PROGRAM

Maxwell E. Shauck, Grazia Zanin and Sergio Alvarez

The initial purpose of the program conducted at the Renewable Aviation Fuels Development Center at Baylor University was the reduction in emissions of the current widely used Jet A fuel. Blend strengths up to 30% Biodiesel by volume were considered and tested for bench properties and for performance in a ground test engine stand. One blend was then selected and tested in a flight testing program conducted in a King Air A90. Results indicate that some emissions-reduction benefits are indeed obtainable. It is also possible to maintain acceptable cold fuel properties in such blends, despite the high freeze point of neat Biodiesels. Biodiesel blends have considerable application as turbine fuel extenders. They have proven suitable as turbine fuels in blends to 20% Biodiesel in flight, and 30% Biodiesel on the ground. The dual constraint to be satisfied is adequate freezing behavior and adequate cold viscosity for fuel spray atomization quality. From a performance standpoint there was no discernible difference between straight Jet A and Biodiesel blends of 80-20 proportions (20% Biodiesel by volume). This is also true for fuel economy, and is borne out by the ground and flight test data gathered during the project. Should petroleum supplies from the Middle East be disrupted, then the existing stocks clearly can be stretched considerably by blending in Biodiesels, which come from domestic feedstocks immune to disruptions. With further investigation, the maximum- practical blend strengths can easily be determined, using the methods defined during this project.

SESSION 2: CRUDE OIL, RESIDUAL FUELS AND COAL I

DEVELOPMENT OF PREDICTION SYSTEM FOR STOCKPILING CRUDE OIL IN UNDERGROUND ROCK CAVERN TANKS

Jun Shigeta, Yutaka Kubota, Takao Hara, Hiroaki Maruyama

Petroleum stockpiling in Japan takes two forms, which are the private sector and government stockpile. Underground oil stockpiling bases for government stockpile were constructed and completed in 1994. Total capacity of underground bases is 5 million kl. Underground stockpiling experience is over ten years at three bases, such as Kuji, Kikuma and Kushikino. Kuji base experienced stocked crude oil level increasing up to about 1 volume % from 1994 to 1999. The vertical sample of stocked crude and bottom water were analyzed but crude sludge and oil-water emulsion were not found. However, we could not clear the problem on sludge and emulsions in rock cavern because the vertical sampling point is only one position of a cavern, which has typically the egg-shaped cross section of 18m widths, 22m heights, and its length is

about 540m. Therefore, Japan Oil, Gas and Metals National Corporation (former JNOC) decided the introduction of the prediction system on Rock Cavern storage. Since 1998, JNOC has developed Crude Oil Sludge Prediction System for above ground tank and floating storage tank as the experimental center of International Sludge Project Group (ISPG) and the system had been completed in June 2001 and now used at 8 storage sites. 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 risk levels. This paper deals with the development of the crude sludge prediction system on underground rock cavern tanks. The evaluation variables and decision tree of Rock Cavern Module will be presented.

NEW ASTM METHOD FOR HEAVY FUEL OIL STABILITY

Hélène Buron and Pascal Bru

A new method, developed by Octel Petroleum specialties and using the Turbiscan, offers an innovative tool for measuring stability of heavy fuel oil. This significant breakthrough could improve the efficiency of critical applications such as monitoring the benefit of additives for upgrading fuel oils or measuring the oil quality in general. This method has recently been granted ASTM approval (ASTM D 7061-04). It involves dilution of the fuel oil in toluene and precipitation of the asphaltenes by heptane in order to simulate the ageing. The asphaltenes precipitation, which is critical for the fuel oil stability, is monitored by the Turbiscan in only 15 minutes through a vertical scanning of the sample every minute. The stability reserve of the fuel oil is directly linked to the phase separation of the asphaltenes detected by the Turbiscan and is measured quickly and easily. The effect of additives in the improvement of fuel oil stability can also be directly investigated using the same method.

ROLE OF ASPHALTENE ON FORMATION OF W/O-TYPE EMULSION FOR STOCKPILING CRUDE OIL IN UNDERGROUND ROCK CAVERN TANKS

Takao Hara, Yoshihiko Kon, Hiroyuki Kumazaki, Kiyomasa Shinbori and Hiroaki Maruyama

Organic sludge deposited during long-term stockpiling of crude oil is entirely composed of n-paraffins of substantially high carbon numbers existing in W/O-type emulsion. Asphaltene fraction involved in crude oil plays a crucial role on the formation of the emulsion. As one of the four kinds of governmental stockpiling system in Japan, crude oil has been stored and sealed by underground-water pressure in an artificial rock cavern tunnel (18m widths, 22m heights and 540m length) since 1994. Because the extent of the oil-water interface has more significant effect on the formation of the emulsion in the rock-cavern system than in the other three stockpiling systems (on-ground tank, in-ground tank and floating vessel), JOGMEC has been paid a particular attention on the behavior of the oil-water interface in the tunnel. Crude oil phase recovered from the interface has been carefully monitored during the stockpiling period and the asphaltene fraction separated from the crude oil phase has been structurally analyzed. The structural parameters of asphaltene concerning to the ability to form stable emulsion are discussed in comparison with those obtained with the other three stockpiling systems. When the bottom water was circulated in the tunnel

in order to maintain the uniform structure of the oil-water interface through the 540m tunnel, thin layer of the W/O-type emulsion phase (water content:7 wt%) was temporarily appeared just after the circulation. The change of the structural parameters of asphaltene is also discussed throughout the circulation operation of the bottom water. In conclusion, the accumulation of the W/O-type emulsion in the interface has not found so far in the rock-cavern stockpiling system.

ACCELERATED TESTING METHOD OF SLUDGE FORMATION FOR STOCKPILING CRUDE OIL IN UNDERGROUND ROCK CAVERN TANKS

Noriaki Yamaguchi, Yoshihiko Kon, Hiroyuki Kumazaki, Kiyomasa Shinbori, Hiroaki Maruyama and Takao Hara

Crude oil has been stored and sealed by underground-water pressure in an artificial rock cavern tunnel (18m widths, 22m heights and 540m length) since 1994, as one of the four kinds of governmental stockpiling system in Japan. Because the extent of the oil-water interface has more significant effect on sludge formation in the rock-cavern system than in the other three stockpiling systems (on-ground tank, in-ground tank and floating vessel), JOGMEC has been paid a particular attention on the behavior of the oil-water interface in the tunnel. The vertical sampling point is only located at the end of the whole tunnel of 540m in length and the behavior of the interface and the base-surface of the tunnel has been monitored through the sampling hole which was drilled at the construction of the tunnel. The property of stored crude oil has also been analyzed on the seldom occasions when a partial portion (nearly, a third) of crude oil filled in a tunnel was discharged out from the cavern for the purpose of training of emergent discharging procedure. The analytical results are discussed on each oil sample which was intermittently collected through a sequence of pumping procedure. As concrete-type spray coating was blown on the surface of the wall of rock cavern, organic sludge including such inorganic particulate might possibly be settled on the bottom of a tunnel in spite of no indication we have ever found. The accelerated testing method for the formation of such heavier sludge than that existing at the oil-water interface is designed and investigated as a function of shear rate between oil and water phase. The result demonstrates that the formation of heavier sludge is negligible under the actual operating condition of rock-cavern storage system.

THE USE OF ENVIRONMENTALLY ACCEPTABLE SYNTHETIC FUEL OILS AND BLENDS THEREOF WITH CRUDE-DERIVED HEAVY FUEL OIL

Paul S. Gravett, Petrus NJ Roets, and Heinrich F. Strauss

Sasol uses two distinct processes in the preparation and manufacturing of petroleum products. These processes comprise of a crude oil derived refinery and a synthetic coal to liquid refinery using Fischer Tropsch chemistry to produce various petroleum products, including residual streams such as fuel oil, that can be used as an energy source in the industry. A distinct characteristic of the synthetic coal derived fuel oils is that it contains basically no sulphur and no heavy metals such as vanadium, aluminium and nickel, which makes it an attractive environmentally acceptable energy source. In contrast, crude oil derived fuel oils

contain high concentrations of sulphur and heavy metals, which will have detrimental affects in certain sensitive burner applications and boilers. The coal derived fuel oils also have the advantage of higher gravimetric energy value compared to the gravimetric energy value of crude oil derived fuel oils. The synthetic derived fuel oils are widely used in South Africa in low to high temperature processes for steam and air heating to manufacture a wide range of materials such as bricks, glass melting, pharmaceutical products and in the food industry. The enforcement of stricter environmental legislation regarding flue gas emissions drives South African industry to use lower sulphur fuels to reduce the effect of the SO_x on the environment. This drive led to research to address and demonstrate the compatibility of Sasol's synthetic derived waxy oils (C18 – C40) and crude derived heavy fuel oils. This research demonstrated the improvement of the pour point of the waxy oil to temperatures below 10°C and the lowering of the sulphur content of crude heavy fuel oil to below 1,5 mass%. The newly synthetic and crude oil derived fuel oil blend is blended under strict production specifications and is used with great success in the South African industry.

SESSION 3: ADDITIVES AND ADDITIVE-RELATED PROPERTIES

DEVELOPMENT OF ADDITIVE CANDIDATES FOR THE THERMAL OXIDATIVE STABILIZATION OF FUTURE JET FUELS AT HIGH TEMPERATURES

Bruce D. Beaver, Caroline Burgess Clifford, Li Gao,¹ and Maria Sobkowiak

We update our studies on the reactivity of a second generation oxygen scavenger, dicyclohexylphenyl phosphine (DCP) in a flowing rig under JP-900 conditions. In addition, we report our efforts to use model systems to further clarify our understanding of the mechanisms by which DCP stabilizes jet fuels. Although these studies are not complete we have significantly strengthened our understanding of the mechanism of fuel oxidative stabilization by DCP

INVESTIGATION OF THE EFFECTIVENESS OF DiEGME TO SUPPRESS SOLIDIFICATION OF WATER IN AIRCRAFT FUEL SYSTEMS

Matthew J. DeWitt, Theodore Williams, Linda Shafer, Richard Striebich, Lee Riehl and Charles L. Delaney

Studies were performed to investigate the effectiveness of Diethylene Glycol Monomethyl Ether (DiEGME) to suppress the solidification onset of water within jet fuel. It has previously been reported that the use of DiEGME as a Fuel System Icing Inhibitor (FSII) can prevent solidification of free and dissolved water within aircraft fuel systems allowing for continued flowability of the fuel and safe operation. However, recent concerns have motivated investigation into whether the continued use of FSII is required or if reduced dose concentrations could be used on an individual platform basis since hardware modifications and improved maintenance practices may have alleviated the previous need. Fundamental and applied studies were performed to improve the understanding of the mechanism by which FSII inhibits the phase-transition rate and onset temperature for water solidification. Specific efforts were made to determine the effect of DiEGME as a function of concentration in water to provide a basis for

required dose rates during application. The experimental methodology employed and results from the various experimental studies will be presented and discussed.

POTENTIAL IMPACT OF DIESEL LUBRICITY ADDITIVES (DLA) ON JET FUEL QUALITY

Dr. Clifford A. Moses, George R. Wilson III, Tracy Boval, and Greg Hemighaus

In January 2005 a lubricity requirement was added to the ASTM D 975 specification for No. 1 and No. 2 diesel fuels in anticipation of low lubricity in Ultra-Low Sulfur Diesel (ULSD) which may be more highly hydro-treated. This requirement will result in the addition of diesel lubricity additives (DLA) into these fuels. The chemistries of these additives are different from the chemistries of the corrosion inhibitors used to provide lubricity improvement in aviation turbine fuels. Further, the diesel lubricity additives are not approved for use in the aviation turbine fuels. The concern is potential contamination of aviation fuels while being transported in fungible pipeline systems from point of manufacture to point of use. Further is the lack of information concerning the hot fuel system carbon fouling which might occur should the diesel lubricity additives (and their associated ULSD) become co-mingled in the aviation turbine fuels. Although the concern for co-mingling is currently limited to the United States and its fungible pipeline system, and although these fuels are more segregated in other parts of the world, there is always the concern that the overseas distribution systems could be changed depending on the economic benefit and overall fuel specification compatibility. This paper reviews the results of laboratory screening tests with DLA's of three basic chemistries to evaluate their effect on thermal stability, lubricity, water separation, electrical conductivity, and pipeline corrosion. The results show that some of the additive chemistries are more detrimental than others and while some fuels are sensitive, others are not.

EXTENDED STABILITY OF AQUAZOLE[®]: A WATER IN DIESEL FUEL EMULSION

Leire ORO URREA Frédéric TORT

Water in diesel fuel emulsions are an alternative fuel dedicated to urban captive fleets and an immediate substitute for diesel fuel, since they do not require modification of engines or logistics.

The physicochemical effects of this kind of fuel in combustion are well known: the mass of water injected increases the speed of the air/fuel mixture, the microexplosion of water droplets ensures better dispersion of the fuel in air, and water vaporisation leads to lower combustion temperature (reduction of nitrogen oxides) and reduced local heterogeneity (soot reduction). The most important parameter to be optimised in the emulsified diesel formulation is the thermal and storage stability of the mixture of the three components: water, diesel fuel and surfactants.

Different tests have been developed to evaluate and optimise the stability of the emulsion:

- grain size
- centrifugation,
- static stability at low, high and room temperature
- dynamic stability at low and high temperature

Furthermore, with new engine technologies (common rail, injection pump), the stability of the fuel at very high temperatures (= 100°C) and high pressures (= 1500 bar) becomes critical and it is necessary to verify its performance through time under these conditions. The rheological behaviour of emulsified fuel has been studied at high pressure and temperature and compared to standard diesel fuel.

SESSION 4: AVIATION FUEL STABILITY

KEYNOTE ADDRESS: JET FUEL – FUTURE SUPPLY INTEGRITY ISSUES (FSII)

Anthony Kitson-Smith

The Global energy market is set to grow over the next 25 years and within this overall growth, the aviation fuel demand is predicted to remain strong and aligned with GDP growth. The introduction (Part I) will review the global energy growth trends to 2030 looking at GDP, energy demand, regional variations and the development of alternative energy sources. Part 2 will switch focus onto the growth in the demand for aviation turbine fuels, the state of the current market and the regional imbalances leading to greater movement of bulk fuels. In the conclusion (Part 3), the discussion covers the hazards of bulk movement of fuels and graphically details the problems with supply interruption arising from dirt, water, surfactant and microbiological contamination. New approaches to dealing with these problems are suggested.

THERMAL STABILITY OF JET-A1 AND MODEL FUELS IN OXIDATIVE CONDITIONS.

C. Hein, M. Sicard, F. Ser, D. Brodzky C. Sayag, G. Djéga-Mariadassou

In modern aircrafts, on board fuel is not only used for propulsion and enhanced global performance but can also be considered as primary coolant. In the fuel system and injection device, a great thermal load can be transferred to the fuel. This thermal stress leads to the formation of gums and solid deposits that cause fouling of nozzles and heat exchangers. The aim of this work consists in the study of Jet-A1 and model fuel (paraffins, aromatics and olefins compounds alone and mixed) oxidation during thermal stress. This thermal stress is carried out in two types of reactors: 1) A backward surge device (atmospheric pressure, 185°C) with air flowing to exacerbate the oxidation phenomena; 2) A bomb type reactor (40 bar, 280°C) with nitrogen and air as pressure gas to be in the nearest operational conditions (temperature and pressure) of a fuel system. Stressed liquid phases have been characterized using visible UV, GC/MS and HPLC. Solid deposits have been characterized by SEM, TEM, HPLC and IR spectrometry. Gases coming from the bomb type reactor and flowing in the backward surge device could be collected and analysed by IR spectrometry and GC. With this series of characterization, it was possible to find oxidation products such as ketones, alcohols and carboxylic acids in the three kind of degradation products (solid, liquid and gas). Besides, the experiments are conducted through several duration to follow the degradation steps, to define and validate oxidation mechanisms.

DE-OXYGENATION SYSTEM FOR INCREASING THERMAL STABILITY OF LOGISTIC FUELS

Santosh Y. Limaye, Donald Koenig and Wesley Jung, Robert Morris and Jeramiah Miller

Logistic fuels tend to form various deposits at relatively low temperatures due to oxidative reactions between the fuel and dissolved oxygen (from fuel exposed to air during fuel handling). This deposition can be minimized or eliminated by either using additives that suppress thermal oxidative reactions, or by removing the dissolved oxygen in the fuel. Fuel additives provide limited gains in thermal stability (225°F) and increase the complexity, whereas the thermal stability of de-oxygenated fuels can be increased by as much as 900°F. Development of thermally stable fuels has significant benefits for military and civilian applications. Specially, for military applications, thermally stable fuels will: (a) allow cooling of turbine components while maintaining higher turbine cycle temperature, (b) increase thrust-to-weight ratio, (c) reduce maintenance, (d) remove the need for specialty fuels, and (e) reduce take-off weight. Phyre Technologies, Inc. has developed a proprietary and unique de-oxygenation system which is capable of reducing the dissolved oxygen levels below 1 ppm. This technological breakthrough is expected to yield compact, lightweight and highly efficient fuel de-oxygenation system suitable for increasing the thermal stability of the jet fuels as well as commercial fuels such as diesel and kerosene that are used in stationary turbine generators. In this paper the overall design of the equipment, operating conditions and results of initial testing of diesel fuel will be discussed.

THE EFFECT OF LONG- TERM STORAGE ON JET FUEL IN AIRCRAFTS

Moshe Rabaev, Daniela Shapira, Josefa Ben-Asher

The effect of long-term storage on jet fuel in aircrafts, while stored in small volume aluminium containers (30 L), was studied over a period of 24 months. A separate study was needed because, most of the literature dealing with aging of jet fuel, considers the outcomes of the long-term storage in relatively larger metal containers. However, in small containers the area to volume ratio is higher, which can lead to different consequence in the aging process. In this study the jet fuel, during its aging progression, has been tested for compliance with MIL- DTL- 83133 specification, peroxides content, potential gum development and the presence of microbiological contamination. In most of the tested parameters there were merely a few minor changes. However, there was a significant elevation in both, flash point and initial boiling point, in the tested jet fuel while aging. Similarly, there was an increase in the acid content. WISM values were not significantly altered. Surprisingly, it was discovered that the thermal stability, as tested by JFTOT, failed to meet the above-mentioned specification. In order to resolve this deviation spectrometric analysis was performed. No correlation was found between metal content and JFTOT results. Next, we analyzed a sediment found in stored jet fuel, but again, its composition could not be linked to the thermal stability results. The fuel flow course in the relevant aircraft system was characterized. As a result, it was realized that relatively poor thermal stability has little impact of the jet engine in this specific system. Finally, it was concluded that in this particular system the aged jet fuel maintained its basic and critical features. The high area/volume ratio didn't enhance the aging of fuel over the period tested in this study.

MEASUREMENT OF KEY SPECIES AND DEVELOPMENT OF A CHEMICAL KINETIC MODEL TOWARD THE PREDICTION OF JET FUEL THERMAL STABILITY

Steven Zabarnick, Zachary West, Nick Kuprowicz, Lori Balster, Jamie Ervin, Donald Minus, and Richard Striebich

The production of detrimental carbonaceous deposits in jet aircraft fuel systems results from the involvement of trace heteroatomic species in the autoxidation chain which occurs upon fuel heating. Although it has been known for many years that these sulfur, nitrogen, and oxygen containing species contribute to the tendency of a fuel to form deposits, simple correlations are not able to predict the oxidation rate or the deposit forming tendency of a range of fuel samples. In this work we employ a series of novel analysis techniques to measure a range of key fuel species classes, such as hydroperoxides, reactive sulfur species, reactive nitrogen species, and polar phenols. These measurements are performed in range of both unreacted and thermally stressed fuel samples. These analyses, along with the measurement of fuel oxidation and deposition, are used in the development and validation of a chemical kinetic model for the prediction of the oxidation and deposit rate. The goal of this work is to elucidate the reaction pathways which determine the oxidation and deposition characteristics of jet fuel samples. Ultimately, combining further refinement of the analysis techniques and model with computational fluid dynamic techniques should allow the prediction of the location and quantities of deposition in aircraft fuel systems.

CORRELATIONS OF NOZZLE FOULING TESTS WITH LABORATORY TESTS OF FUEL THERMAL STABILITY

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

During the recent program to evaluate the effect of red dye on fuel thermal stability and fuel system component fouling, 19 commercial jet fuels were evaluated for thermal stability with a number of laboratory-scale deposition tests. These fuels represented various crude sources and refining histories. This paper compares the results of those deposition tests with each other as well as with the results of fuel-nozzle fouling tests. The results indicate that the JFTOT may have been underrated because of its inability to quantify deposits. Breakpoint temperature is shown to correlate very well with nozzle fouling rates. Deposit mass on JFTOT tubes correlated reasonably well with breakpoint, but other popular tests evaluated were poorly correlated the breakpoint temperature and by inference with nozzle fouling tests. A strong correlation of JFTOT deposit thickness at a single temperature with breakpoint temperature suggests a potential screening test for thermal stability issues with additives and contaminants.

OXIDATION OF JP-5 IN SINGLE AND MULTIPASS FLOW TESTING

Robert E. Morris, Thomas Evans, Janet M. Hughes, John E. Colbert and Clarence J. Nowack

The Navy single tube reactor (STR) was employed to examine the impact of copper contamination on fuel oxidation over a range of bulk fuel temperatures that encompass aircraft system design temperatures. An alternative STR design was employed to provide a

means to thermally stress the fuel in a closed system, during single- and multi-pass (recirculating) experiments. In this manner, fuel autoxidation in the STR was compared with the standard JFTOT. In general, the extent of autoxidation in the JFTOT was greater than in the STR at equivalent bulk fuel temperatures, which is consistent with differences in flow rates and residence times. Copper was innocuous in promoting the formation of thermal deposits in the STR at bulk fuel temperatures below approximately 170°C. At higher temperatures, oxidation rates increased dramatically, with concurrent deposition rate increases. Under these conditions, when the fuel contained dissolved copper, the copper was partitioned into the thermal deposits. This concurrent copper depletion continued during multipass testing until all the available oxygen was consumed and autoxidation ceased. However, at these temperatures, in the presence of a metal deactivator additive (MDA), all the copper remained in solution as the Cu-MDA complex. The findings of this study indicate that as bulk fuel design temperatures continue to increase, copper-contamination may begin to be a greater factor in contributing to the accumulation of deleterious thermal deposits in regions of slow flow. However, these results also indicate that additives containing metal deactivators may play a useful role in mediating the impact of copper contamination on thermal deposition within fuel system components.

SESSION 5: MICROBIAL

MICROBIAL DEGRADATION OF FIBER REINFORCED POLYMERIC COMPOSITE SYSTEMS

Howard L. Chesneau and Edward W. English

The versatility and unique properties of fiber reinforced polymer (FRP) composites have been the sole impetus for its increased use in a variety of industries and applications including hydrocarbon storage systems. Associated with the use of FRP composites has also been the unexplainable observation of sustained microbial growth in diverse applications such as space stations, marine shipping, aircraft, sewer pipes, medical devices, etc. Historically, it was difficult to accurately characterize the type of deterioration and the impact of microorganisms on FRP composites. This has led to the mistaken notion that these materials are not subject to the same deterioration that plague steel tank systems. However, with the introduction of new analytical techniques coupled with sound traditional methods, researchers now have the ability to accurately characterize the impact microorganisms have on a variety of FRP composite systems within a short period of time. This paper will cover both the risks as well as the current research concerning microbiological attacks on FRP systems.

INVESTIGATION OF THE HYDROCARBON DEGRADATION MECHANISMS OF *Bacillus Licheniformis* STRAINS ISOLATED FROM UNITED STATES AIR FORCE AVIATION FUEL TANKS

Capt. Michelle E. Rauch, Ph.D.

While the ability of microbes to contaminate aviation fuel tanks has been long known and

is historically well-documented, the contemporary understanding of the organisms inhabiting modern fuel tanks and their metabolism mechanisms is rudimentary. A greater comprehension of the bacteria and fungus populating and degrading aviation fuel will give rise to new methods of detection and prevention. In a 2002-2003 study of microbial contamination of United States Air Force (USAF) aviation fuel tanks, the bacteria, *Bacillus licheniformis* was found to be the most prevalent organism; isolated from tanks at seven of the eleven bases sampled. Previous literature describes several *B. licheniformis* strains isolated from oil wells and their ability to synthesize a biosurfactant, lichenysin A. Biosurfactant production is hypothesized to facilitate the proliferation of other fuel tank microorganisms by liberating hydrocarbons from the fuel phase and making the compounds accessible for metabolism. The *Bacillus licheniformis* mechanism of petroleum biodeterioration has been investigated including protein isolation, enzymatic studies and the organism's microbial induced corrosion effects on aluminum alloys.

INVESTIGATION OF THE ANTI-MICROBIAL CHARACTERISTICS OF DI-ETHYLENE GLYCOL MONO METHYL ETHER (Di-EGME) IN RELATION TO ITS USE INTERMITTENTLY AND AT SUB-LETHAL CONCENTRATIONS

Graham C. Hill, Edward C. Hill and Steve Anderson

The secondary benefit of using the fuel system icing inhibitor (FSII) mono-ethylene glycol mono-methyl ether (EGME) for controlling microbial growth in fuel tanks and systems has been well documented. Only a few studies have investigated the anti-microbial properties of di-ethylene glycol mono-methyl ether (DiEGME) which, on account of its preferable toxicological profile, has largely replaced EGME as the FSII of choice. These studies suggest that there may be a mild toxic and osmotic anti-microbial effect. None of the studies fully investigate the impact of sub-lethal concentrations or intermittent exposure of microbes to DiEGME. In many aircraft operations it will be impractical to guarantee a continuous full dose of DiEGME in all fuel uplifted. Further, where DiEGME is applied upstream rather than at point of use, it is probable that leaching to water phase in the distribution chain may result in sub-lethal concentrations of DiEGME delivered to aircraft. Experience tells us that exposure of microbes to sub-lethal concentrations of an anti-microbial agent can result in development of tolerant or resistant strains. The potential impact of sub-lethal and intermittent use of DiEGME on microbial growth in fuel systems, was considered in the following study which investigated growth/tolerance/kill of microbes in water containing progressively increasing concentrations of DiEGME, and the effect of intermittent use of DiEGME.

CHARACTERIZATION OF THE BIO-BURDEN IN UNITED STATES AVIATION FUEL USING DIRECT POLYMERASE CHAIN REACTION (PCR) AND OTHER ANALYTICAL TECHNIQUES

Sarah K. Chelgren, Tracy R. Denaro, Lori M. Balster, Marlin D. Vangness, and Jara N. Lang

The natural presence of microorganisms in jet fuel can cause gradual degradation of aircraft and fuel handling systems, a fact which has been well-documented for over forty years. Because the presence of microorganisms continues to cause fuel system problems today, it is thus necessary and desirable to continue development of analytical techniques for the most efficient and thorough characterization of these organisms. This paper presents results from an ongoing study to characterize the bio-burden in Air Force fuel systems, including a broad range of aircraft, fuel storage tanks, and fuel delivery systems located across the continental U.S.

Traditional microbiology methods have been used successfully in the past to isolate microorganisms from fuel samples. Unfortunately, these methods do not take into account unculturable microorganisms and numerous other factors introduced with the drastic environmental change from the microorganism's fuel environment to a standard microbiological media plate. In this study, microorganisms were isolated from each fuel sample using both a direct polymerase chain reaction (direct PCR) method and traditional microbiological culture methods. The isolated microorganisms were further identified using Gas Chromatograph Fatty-Acid Methyl-Ester Profiling (GC-Fame) and 16S & 18S Ribosomal RNA Sequencing. Quantification of microorganisms by various commercial test kits was also explored, and the results were compared to those obtained by GC-Fame and rRNA Sequencing methods. Through the refinement and comparison of these analytical techniques, the microorganisms present in aviation fuel systems were better characterized to achieve a more accurate picture of the bio- burden, including its composition, location, and activity.

STABILITY OF LIGHT STRAIGHT RUN DIESEL FUEL, SUPPLEMENTED WITH PRESERVATIVE ADDITIVES, DURING LONG TERM STORAGE IN COMBAT VEHICLES

Geva J, Schuftan M, Geissmann E., Sapir J. and Fass R.

The "Israeli Defense forces" (IDF) keeps fully fueled Diesel propelled vehicles in long-term storage, under controlled humidity, for up to 2.5 years. The length of the storage period was dictated by results of a long-term survey on the fate of stored straight run diesel fuel under storage conditions resembling conditions at the end user level. The survey revealed that risky deterioration processes start to occur within the third year of the storage. Since the refreshing procedures are very costly it was important to increase the refueling interval. This may be achieved by adding stabilizing and biocidal additives to the stored fuel. Several commercial additive packages approved for use in diesel engines, were tested for their efficiency in lab scale experiments and in real underground small storage tanks. The best effective package was applied in a long-term storage field test. The field test was carried out with 22 combat vehicles with pre-cleaned fuel tanks that were refueled with additives supplementing diesel fuel. The vehicles were stored under humidity control at ambient conditions and were sampled for microbial activity and chemical deterioration analyses twice a year for 5.5 years. The results have shown that the additive supplemented Diesel fuel preserved its chemical quality for up to 5 years. A fast chemical deterioration occurred in 5 out of 22 vehicles during the following 6 months. No biological activity was determined in the vehicles' fuel tanks throughout the duration of the experiment. We concluded that Straight Run Diesel Fuel, supplemented with stabilizers and biocides, can be stored under these conditions for up to 5 years.

RELATIVE BIODEGRADABILITY OF B-100 BIODIESEL AND CONVENTIONAL LOW SULFUR DIESEL FUELS

Frederick J. Passman, Ph.D., Jason K. Dobranik, Ph.D.

The paper presents the evaluation of four fuels for their relative biodegradability. The fuels evaluated included two biodiesel (B-100) products: untreated 100% coconut methyl ester (CME-100) and microbicide-treated CME-100; and two conventional diesel products: low sulfur diesel (LSD) and additized LSD. Relative biodegradability was determined by evaluating the changes in a set of parameters during the course of 90-days exposure to

an uncharacterized mixed microbial inoculum. Microcosms (3.8 L glass jars) contained 2 L fuel over 200 mL synthetic bottom water. Contaminated LSD over bottom-water was used as a positive control. Filter-sterilized CME-100 over sterile bottom-water was used as a negative control. Fuel phase parameters included: ATP, bacteria and fungi colony counts, total acid number, Karl Fischer water, corrosivity and appearance. Bottom-water parameters included: ATP, two-hour oxygen demand, bacteria and fungi colony counts pH, alkalinity/acidity, total dissolved solids, total organic carbon and gross appearance, including invert emulsion/biofilm presence and morphology.

SESSION 6: DIESEL FUEL, GASOLINE AND HEATING OIL

Keynote Address:

CURRENT AND FUTURE DIESEL FUEL ISSUES IN THE UNITED STATES

Manuch Nikanjam

Diesel fuel in the U.S. has been mostly an uneventful product for many years. Due to recent pressure to provide fuels that are compatible with new engine technology to reduce emissions, and to improve performance and sociability of diesel vehicles, a number of changes have been made or are being considered. The potential for the introduction of light-duty diesel vehicles also has created challenges that are unique to the U.S. This presentation summarizes the cultural differences between the U.S. and other regions of the world such as Europe, and will list fuel properties and issues that need to be considered as a necessary part of a transition from “business as usual” to the new and more challenging environment.

FUEL QUALITY CHALLENGES IN A MARINE ENVIRONMENT: A UNITED STATES COAST GUARD PERSPECTIVE

Sherry Williams, Thomas Gahs

The United States Coast Guard (USCG) has a multifaceted mission that requires different fuel needs than that of the US Navy or commercial ships. Mission locations, schedules and cost prohibit the Coast Guard from solely lifting military specification fuels and instead require them to rely heavily on commercial marine middle distillate fuel. However, ship and engine design require a high quality, more rigorously tested fuel than what may be available at some commercial ports. Two classes of USCG cutters utilize gas turbine engines for shipboard propulsion. Many commercial marine specifications require limited or no testing of chemical and physical properties that may affect the gas turbine, such as trace metals, or allow higher limits on critical properties, such as carbon residue. Additionally, the storage stability characteristics of the commercial fuel affect all cutters, regardless of their prime mover type. As a result, in 1999, the Coast Guard joined an ongoing Defense Energy Support Center (DESC) in-line bunker-sampling program. The goal of this program is to monitor the quality of commercial fuel being burned by USCG cutters and to provide real-time guidance in the event an off-specification fuel is lifted. This is a joint effort with the DESC and the US Navy, to monitor the quality of commercial marine middle distillate fuel being lifted by

USCG cutters. Fuel is collected via a drip sampler at the cutter's deck riser connection, which is generally considered to be the fuel custody transfer point. A continuous drip sample is taken during the entire refueling evolution and then transferred to a sample can for shipment to the lab. Since 1999, over 300 in-line samples have been tested from a worldwide variety of ports. As a result of this on-going program, the Coast Guard has been able to limit the negative effects of any off-specification fuel and also expand their use of commercial fuels in gas turbine powered ships, thus providing a cost savings. The Coast Guard has also seen an improvement in bunker fuel quality at ports where they have lifted off-spec fuel and reported those results back to the contractor. The intent of this paper is to provide an overview of the data collected on commercial marine bunker fuel, in relation to the military specification requirements and needs of the USCG cutters.

SASOL SLURRY PHASE™ FISCHER-TROPSCH CONDENSATE AS STRAIGHT RUN DIESEL BLENDING COMPONENT WITH SASOL SLURRY PHASE DISTILLATE™ DIESEL

Delanie Lamprecht, Petrus NJ Roets and Heinrich F. Strauss

The Sasol Slurry Phase Distillate™ (SPD™) Low Temperature Fischer-Tropsch (LTFT) process is a well known process in which carbon monoxide and hydrogen are reacted over a cobalt containing catalyst to produce a mixture of straight and branched chain hydrocarbons and oxygenates. These LTFT products are hydroconverted into a range of final products where the heavy distillates are hydrocracked and the olefins and oxygenates are hydrogenated to form a final product that is highly paraffinic. It is known that trace amounts of oxygen and nitrogen containing compounds that are naturally present in petroleum derived diesel fuel contribute to good boundary lubrication and that lubricity additives are needed to compensate for poor lubricity of severely hydrotreated fuel. As an alternative to adding a lubricity additive, un-hydrogenated Sasol Slurry Phase™ (SP™) Fischer-Tropsch (FT) condensate can be blended as a straight run diesel with the hydrocracked SP™ FT wax to improve the lubricity properties of the Sasol SPD™ diesel fuel properties such as storage stability, cold flow properties, cetane number and viscosity was also investigated.

STABILIZATION OF DOMESTIC HEATING FUEL TO ADAPT IT TO THE NEW REQUIREMENTS OF THE MARKET

*Jesús Delgado Diestre *1, Laura Arrabal Flores 2*

The increasing use of conversion streams in domestic heating fuel, as a result of the demanding diesel fuel specifications, makes worse and worse their stability, with the consequent dissatisfaction of the user. The received claims and the composition of heating fuels have been analyzed. In most of the cases they are associated to fouling (combustion/injectors, blocking, dirt) whose probable cause is the instability of the product. The use of the fuel, the type of installation, common habits has been analyzed, and it is seen that influence decidedly in the stability of the product. The increase of the component of conversion in the domestic heating fuel has been confirmed; nevertheless, the claims are not function of the percentage of conversion, so that it has looked for by some more influential

factor. The influence of the hidrotratamiento of the conversion current has been verified that is gotten up. Also, it has been determined the interactions between the currents of direct distillation, the hidrotreating streams and conversion components. These interactions are complex, as it is expected because the complexity of mechanisms of instability. Different systems from aditivación have been evaluated. Most of the reaction routes leads to insoluble products, for that reason the dispersing products usually are very effective. However, also there are routes of gums formation that requires an antioxidant one. The estabilizing additives affect neutralizing acids product of the oxidation. The metals (Zn, Cu) can accelerate the oxidation mechanisms, so that it is necessary to use metal deactivators if there is presence of such. A combination of estabilizing components has been selected that guarantees good behavior of the product, independently of its origin and the form of use, within reasonable and habitual limits. The solution has been applied to the Spanish market, with results that to date are excellent and they will be possible to specify better at the end of winter 2004-2005.

USE OF SYNTHETIC FISCHER-TROPSCH (FT) LIQUID FUELS FOR ARMY GROUND EQUIPMENT

Leo L. Stavinoha, Patsy A. Muzzell, Brian McKay, and Coryne A. Forest

This paper provides data for FT fuels produced by Syntroleum to meet Syntroleum FT production specifications for transportation type fuels used in diesel compression ignition engines and turbine engines (ground, aviation, and electrical generator). Salient characteristics of commercial item descriptions (CID) for procurement of fuels (both neat FT fuel and blends of FT fuel with petroleum derived fuel) are provided. The types of fuel included are diesel (grades 1 & 2), kerosene (illumination and heating burner applications), and aviation turbine fuel, as defined in American Society for Testing and Materials International (ASTM International) specifications. The General Services Administration (GSA) has authorized the use of CIDs for all federal agencies and provides a mechanism for procurement of fuels meeting ASTM specifications and other requirements specific to the CID. Examples of CID include A-A- 59693A (January 15, 2004) "Commercial Item Description for Biodiesel (B20) Diesel Fuel and A-A-52557A (January 16, 2001) "Commercial Item Description for Fuel Oil For Posts, Camps and Stations." A salient feature of A-A-52557A is that the grades of diesel fuel oils therein specified are hydrocarbon oils conforming to the detailed requirements of ASTM D 975 (Standard Specification for Diesel Fuel Oils). Since modern FT fuel technology utilizes processes that result in "clean" liquid fuels that contain no sulfur and no aromatics, any fuel system or component that rely on fuel aromatics for swell of elastomeric seals and gaskets may leak fuel or otherwise fail to perform when this FT "clean fuel" is utilized. Additionally, it also lacks qualification and approval for use in sensitive (aircraft) systems. During the CID development and coordination within DoD (Army, Navy, and Air Force), component qualification testing and demonstration/approval testing in selected fleets can be done to validate the draft CID for publication. Civil Agency Coordination for the CID includes GSA, HHS and DOT.

OXIDATION STABILITY OF GASOLINES, PRODUCED IN CONFORMITY TO EUROPEAN REQUIREMENTS AT “LUKOIL-NEFTOCHIM-BOURGAS”

G. N. Andonov, A. S. Ivanov, and S. K. Ivanov

The concentrations of natural inhibitors and the rate of initiation for the oxidation processes of gasoline from catalytic cracking (FCC) and catalytic reforming (CR) are measured. The storage period of 24 months on this basis was predicted. The content of carboxylic acids and gum products grows up with the increase of alkenes content in gasolines. A period of accelerated accumulation of oxidation products is detected. The investigation carried out in the work confirm the presence of natural inhibitors in FCC gasoline and in those produced from 10% CR gasoline and 90% FCC gasoline. It is proved that $x \cdot 10^{-4}$ mol/l of natural inhibitors are consumed at storage in glass apparatus in dark at temperature of 20°C for three months and thus a storage term of 24 months is predicted. A period of accelerated accumulation of carboxylic acids and gum products is observed. The content of the latter grows up with the increase of the alkenes content in gasoline. The obtained results give the possibility, after additional experiments, to create suitable nomograms on the basis of which the induction periods and storage term at known group composition may be calculated.

PREMIUM DIESEL FUEL IN NORTH AMERICA: HOW CLOSE ARE WE? A PERFORMANCE TESTING SURVEY OF WINTER FUELS FROM 2004-2005

Benjamin R. Forester and David R. Forester

After the loss of detergency performance evaluation by the L-10 test, NCWM revised its premium diesel specifications in North America to the following four performance criteria: (1) Cetane Number - ASTM D 613 or Cetane Index D4737; (2) Low Temperature Operability - ASTM D 4539 LTFT, ASTM D 2500 CP or ASTM 6371 CFPP; (3) Thermal Stability – ASTM D 6468 (180 min., 150°C) and (4) Lubricity – ASTM D 6079. During the winter months of Oct 2004 to March, 2005, Power Service Products obtained over 400 untreated “regional diesel fuel samples” from all regions of North America. These fuels were #1 and #2 S500 and #2 S5000 fuels. These fuel samples were evaluated for the above premium diesel performance parameters using cetane index, CFPP, thermal stability and HFRR. Also, various additives were evaluated to improve low temperature operability, thermal stability and lubricity in order to help meet premium specifications. With the significantly expanding light and medium duty diesel market in North America, the need for premium quality fuel is already growing significantly. This poster will present the data from these extensive evaluations, as well as regional trends to help answer the question, “How close are we to truly premium diesel?”

SESSION 7: CRUDE OIL, RESIDUAL FUELS AND COAL II

DEMULSIFIERS AND CRUDE OIL EMULSION: CORRELATION EFFECT TO THEIR COMPOSITION AND PHYSICAL PROPERTIES

Yekhlef Elomrani, Muftah Darwish, Layla El-hamrani, and Aisha El-heshani

Characterization of some crude samples has been thoroughly characterized including

Asphaltene, Resin, Wax, and Oils in addition to water content. The physical properties were determined for these which are: total acid number, density, and viscosity. The density of water content in the crude oil emulsion was determined for the seek of comparison. Several methods are used to break water oil emulsions. This work concentrates on using demulsifiers as one of the best methods for breaking emulsion and separating the two phases from each other, if an appropriate condition were taken into consideration. The search for an appropriate demulsifier is generally carried out through the well known “Bottle Test” technique. An approach is proposed here, which is based on earlier work on the rate of separation of water- hydrocarbon mixtures. The efficiency of demulsifiers tested depends on the variation of salinity, temperature, crude oil type and the demulsifier concentration. Water content in the crude oil emulsion could be separated by different techniques, which are: a) Mechanical means or agitation, which increases the collision number between particles and their coalescence. So it will separate the free water from the crude oil emulsion; b) Dispersed water could be separated by distillation “ASTM D 4006”; c) Water content could be separated by Bottle test method, this method used to evaluate the efficiency of the demulsifier used.

THE NATURE OF NAPHTHENIC ACIDS IN ATHABASCA BITUMEN AND THEIR FATE DURING THERMAL CRACKING

Parviz Rahimi¹, Ryan Rodgers², Alan G. Marshall², Alem Teclerariam¹, Kamran Akbarzadeh¹, and Theo de Bruijn

Naphthenic acids are typically defined as carboxylic acids with single or multiple saturated cyclic rings. In most cases, however, the naphthenic acids refer to all organic acids in crudes that have acidic functionality even though they contain aromatic moieties. Although methods are now available to isolate and quantitatively determine naphthenic acids directly, most laboratories use ASTM D-644 to determine total acid number (TAN) that measures all acidic components of the crude. To measure the acidity of the crude due to only naphthenic acids, UOP has developed a method (UOP –565) that includes an extra step for removing sulfur compounds other than naphthenic acids that contribute to the acidity of crudes. Although not all acidic components in crudes are potentially corrosive, refineries would like to process crude with TAN of <0.5 mg KOH/g oil and streams containing TAN <1.5 mg KOH/g oil. Athabasca bitumen has been shown to have a TAN of ~3.2-5.5 mg KOH/g oil, i.e., well above the accepted limit. It is not clear, however, how much (if any) of this increased TAN contributes to the corrosivity of refinery equipment.

Athabasca bitumen has been characterized in details by many investigators. Combining extensive chromatographic separation and field ionization mass spectrometry (FIMS), a number of carboxylic acids, including acyclic, tricyclic (diaromatic pentacyclic), and tetracyclic (diaromatic hexacyclic) carboxylic acids have been identified. The molecular weights of these acids ranged from 210 Da to >700 Da. Other mass spectrometric techniques including chemical ionization (CI), liquid secondary-ion mass spectrometry (LSIMS), atmospheric pressure chemical ionization (APCI), and electrospray ionization (ESI) have been evaluated for the characterization of naphthenic acids. High-resolution mass spectrometry (HRMS) was applied to identify the acidic species in a California crude oil. More recently high field Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been applied to identify more than 3000 acids in heavy petroleum. This technique was also used to identify naphthenic acids in a variety of crudes and correlated those findings to TAN, corrosivity, and elemental composition. Although Athabasca bitumen has high TAN, naphthenic acid corrosion has

never been reported. It has been postulated that there are two types of naphthenic acids in Athabasca bitumen: low and high molecular weight. According to this hypothesis only low molecular weight naphthenic acids are corrosive, whereas high molecular weight naphthenic acids are not corrosive and may actually inhibit corrosion.

The objectives of this work were: 1) to identify and characterize the naphthenic acid components of Athabasca bitumen by different mass spectrometry techniques; 2) to demonstrate whether any type of prior separation including distillation and/or chromatographic separation is necessary for detailed characterization of naphthenic acids in Athabasca bitumen; 3) to compare the characteristics of the naphthenic acids found in Athabasca bitumen with those found in other crudes known to be corrosive; 4) to investigate kinetics of thermal degradation of naphthenic acids by mass spectrometry technique.

DEVELOPMENTS IN MONITORING/CONTROLLING RESIDUAL FUEL OIL QUALITY

Frans G.A. van den Berg and J. D.M. Woldendorp

Fuel oils should meet recognized specifications and moreover, be fit for purpose, i.e. ensure safe and continuous operation in all applications. Unfortunately, current specifications do not cover all possible aspects of fuel performance. Indeed, fuels meeting agreed standard specifications may still cause problems in the marketplace. Various reasons for poor performance will be discussed. Shell Global Solutions is actively involved in developing and standardizing reliable new methods to assist in ensuring that residual fuels delivered to customers are fit for purpose. This paper discusses several analytical tools, which may be feasible for monitoring and controlling RFO quality:

- High temperature boiling point distribution by GC (SIMDIST): this may be used to check for a possible dumbbell or gap type distribution, which may result in a poor combustion quality, both in the engine and in continuous combustion applications.
- Fuel Ignition Analyzer (FIA): this combustion test rig is a better tool to assess fuel oil ignition quality than indirect correlations such as the CCAI (Calculated Carbon Aromaticity Index), especially for medium-speed engines.
- Polypropylene filtration test: this specially developed filtration test may be used to check for polypropylene particles which can result in severe filter plugging.
- IR and GC-MS methods: These were specifically developed to detect the presence of non-petroleum derived components such as biofuels, which are not allowed for marine applications and may cause filtration and corrosion problems when mixed with conventional fuels.

SESSION 8: BIODIESEL

MICROBIAL CONTAMINATION OF BIODIESEL AND BIODIESEL BLENDS

Howard L. Chesneau and Edward W. English

Over the past decade, the United States and Europe have experienced a continual increase in the use of biodiesel as a fuel or blend stock for diesel fuels. Along with the number of positive benefits derived from the use of biodiesel there are also problems associated with biodiesel in the presence of water. Due to its structure as well as the lack of aromatic compounds biodiesel has a greater propensity and susceptibility to microbial contamination. As a blend stock, biodiesel can increase the probability of microbial contamination of low sulfur diesel fuels as well as the ultra-low sulfur diesel fuels. Microbial contamination of fuels is responsible for pitting corrosion of fuel storage tanks, intergranular attack of certain metals, filter blockage, and product spoilage. This presentation will focus on the vulnerability of biodiesel systems to microbiological attack over and above regular diesel fuel.

PREDICTING THE SWELLING EFFECTS ON ELASTOMERS OF BIODIESELS, BIODIESEL-PETROLEUM DIESEL BLENDS AND A SYNTHETIC AVIATION FUEL

Janice I Hetherington and Stephanie Green

In Europe biodiesels made from rape seed methyl ester or reconstituted cooking oil are available for automotive use. Most frequently the biodiesel is used in a blend with petroleum diesel. The swelling characteristics of eleven elastomers in both types of biodiesel, petroleum diesel and several biodiesel-petroleum diesel blends have been measured until equilibrium swelling was achieved. The measured swelling characteristics are compared with predictions made from solubility parameter theory. Similar swelling measurements and comparison with predictions have been made with a hydrocarbon mixture that is representative of a synthetic jet fuel.

BIODIESEL OXIDATION STABILITY BY PRESSURE DIFFERENTIAL SCANNING CALORIMETRY

Leo L. Stavinoha and Kathryn S. Kline

This report summarizes experiments with oxidatively reactive methyl soyate biodiesel fuels obtained from different suppliers using different manufacturing processes. Two modified test methods, ASTM E 2009, Standard Test Method for Oxidation Onset Temperature of Hydrocarbons by Differential Scanning Calorimetry, and ASTM D 6186, Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC), were employed as rapid tests to correlate to a series of biodiesel samples having a range of stability. Three antioxidants were evaluated for effectiveness and blends of biodiesel in diesel fuel were evaluated using PDSC. The antioxidants were Butylated Hydroxy Toluene (BHT) at 240 mg/L, Tertiary Butyl Hydroxy Quinone (TBHQ) at 240 mg/L, and Tenox 21 at 1000 mg/L. Advantages of the ASTM E 2009 method are demonstrated by the ability to get onset temperatures for the biodiesels as well as blends with diesel and the neat diesel and rank the antioxidant effectiveness.

SESSION 9: ANALYTICAL METHODOLOGY

CORRELATION OF OPTICAL TEST METHODS FOR AVIATION TURBINE FUELS

Alan R. Kramer and Mark Ferrell

Optical methods for determining deposit thickness on pre-heater tubes are explored for accuracy, precision and correlation. Spectroscopic ellipsometry (SE), laser ellipsometry (LE) and visual inspection (ASTM Test Method D1660) techniques are applied to a range of pre-heater tubes with normal and abnormal ratings to characterize deposit thickness and profiles. Modeling for SE and LE are presented using effective medium approximation (EMA) and pseudo dielectric function methods to properly characterize deposit structure and porosity are also presented.

OBJECTIVE RATINGS OF JFTOT HEATER TUBES - A FORTY YEAR JOURNEY

George R. Wilson, III

In 1965 the Coordinating Research Council (CRC) started a program to replace the CFR Coker, ASTM D1660, with a better method. There were two objectives: 1) develop a smaller device that took far less sample, and 2) develop an objective means of rating Heater Tube Deposits. The first objective was achieved. The result was the Jet Fuel Thermal Oxidation Tester (JFTOT). It became an ASTM method (D3241) in 1972, dominant in the industry by 1980, and the Coker method was withdrawn in 1990. The CRC program met the second objective too but with less stellar results. The objective rating device, the Tube Deposit Rater (TDR), was reliable and easy to use. It achieved a moderate level of success but never made it into the commercial specifications for jet fuel. After two attempts, ASTM asked CRC to try again. After fifteen years of effort the industry may be close to a solution. This paper will discuss this chronology, the reasons for the failures, and the hurdles yet to be cleared in the effort to supplant fifty years of successful visual rating.

DEVELOPMENT OF IMPROVED SENSING TECHNOLOGIES TO MEASURE FUEL QUALITY

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

Currently, fuel quality assessment is performed with a suite of wet chemical and instrumental analyses. An instrumented sensing approach to fuel quality assurance offers significant advantages in analysis time, reduced operating cost and possibly increased accuracy. The Navy advanced fuel sensor development initiative is directed towards the development of automated off-line and in-line fuel property assessment. Historically, characterization of fuels by infrared spectroscopy has been a mainstay of fuels research for over 60 years, and the past 15 years have seen a surge of research focused upon the development of rigorous calibration models that correlate the compositional information contained within spectroscopic data to fuel quality parameters. Spectroscopic methods are desirable for in-line fuel quality sensors due to the relative simplicity of instrumentation, rapid analysis time, and high quality of the data from a chemometric perspective. Chemometric

multivariate analysis of spectroscopic data is desirable due to several reasons. Chief among them is the so called first order advantage, providing the ability to recognize the presence of interferants, calibrate in the presence of known interferants, and conferring the advantages normally provided by signal averaging. While many critical fuel properties can be predicted fairly well with spectroscopy, other properties, such as fuel system icing inhibitor (FSII) concentration, are not adequately measured by a single spectroscopic analysis. This paper describes the development of novel multivariate models to correlate NIR and FTIR data with a range of fuel properties. In those instances where the spectroscopic data were not correlated adequately to a desired property, data fusion approaches were examined by developing multi-dimensional models from an array of multiple sensors.

CHARACTERIZATION OF FUEL BLENDS BY GC-MS AND MULTI-WAY CHEMOMETRIC TOOLS

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

Discrimination of fuel types in mixtures is a common need in remediation of fuel spills and the examination of fuel contamination issues. Available methods for performing these types of discrimination analyses generally rely on either spectroscopic or chromatographic analyses. However, these methods are limited when the compositions of the components of a mixture overlap or are very similar. In this study, we have shown that many of these limitations can be overcome by including the additional dimension of compositional information provided by gas chromatography-mass spectrometry (GC-MS). We have developed novel multidimensional chemometric techniques to analyze GC-MS data and unravel multi-component properties of fuel blends into its component parts. The sensitivity and accuracy of this approach was illustrated by successful quantitative and qualitative discrimination of the components of diesel fuel (NATO F-76) samples contaminated with light cycle oil and with another similar diesel fuel. This approach offers the means to more effectively characterize fuel blends and contaminants, by comparison with the known fuel. If the known fuel components are not available, an estimated discrimination can still be made by comparison with typical specification fuels.

SESSION 10: FUEL FILTRATION AND CLEANLINESS

EFFECTS OF AVIATION FUEL ADDITIVES ON FILTRATION PERFORMANCE

Gary Bessee and Vic Hughes

Southwest Research Institute (SwRI) aviation cooperative research has shown that the GE 8Q462 aviation thermal stability additive (commonly known as +100) is not as detrimental to filtration performance as originally thought. However, there are still questions as to why there is a difference between our data and previously published data. A continuation of the SwRI work is investigating the effects of a static dissipator, corrosion inhibitor, fuel system icing inhibitor, and the GE 8Q462 thermal stability additive and the combination of them in hope of providing a model to predict filtration performance. A half-factorial design of experiment (DOE) has been prepared to perform this research. This paper will present the data

generated to date illustrating what the filtration effects are as a function of these additives.

TEMPERATURE AND SALINITY EFFECTS ON COMMERCIAL FILTER MONITORS

Robert H. Becker

Filter monitors are an important part of the aviation-fuel handling system which ensure fuel is clean and dry when delivered into aircraft. These monitors protect airplanes during refuelling by absorbing free water from the fuel and keeping it from entering onto airplanes. Monitors are typically located at the end of a complex fuel-distribution system, where they function as a final check to keep water off planes. It was discovered in 2002 that filter monitors in service sometimes degrade so that they lose some of their ability to absorb water, which may permit water to pass through them. While testing of monitors, to elucidate this degradation mechanism, continues within the industry, ExxonMobil has tested the effects of salt and temperature on filter monitors to better understand the performance of current commercial products. Two-inch filter monitor models were tested to explore how they performed with elevated salt concentrations and at low temperatures. Temperature variations and salt-laden fuel were chosen as challenges to filter monitor performance because both are known to impact the water absorbing material of filter monitors: superabsorbent polymers (SAPs). Laboratory testing indicates that low temperatures slow the rate of SAP water uptake and elevated salinity deactivates SAP water uptake. The response of commercial filter monitors to these challenges was not known because parameters such as the type and amount of SAP and construction of the element can lead to variations in sensitivity. This paper presents results from single-element-test rig slug testing of commercial two-inch filter monitors at elevated salinities and reduced temperatures to show the range of response in current products. These results are anticipated to form a basis for improved specifications for new products.

THE DEVELOPMENT OF THE 5TH EDITION OF THE API/IP FILTER MONITOR SPECIFICATION

Dennis H. Hoskin

This presentation provides the perspective of the API/IP Filtration Subcommittee Chair on the current status and future direction of the aviation filter monitor specification. Filter monitors, meeting the American Petroleum Institute (API) and Energy Institute (Institute of Petroleum, IP) Specification 1583, are an important part of the aviation fuel handling system that ensures fuel is clean and dry when delivered into aircraft. In September of 2002, the aviation industry learned that the water absorption performance of filter monitors sometimes degrades in service much more than expected. Since then much work has been done to understand the causes and/or mechanisms of degradation. Part of the investigation was to better understand the chemistry of superabsorbent polymers, the component responsible for water absorption performance. Another part of the investigation was to evaluate stresses in the fuel distribution and handling system that may challenge filter monitor performance in field service. This paper provides a brief background of filter monitor construction, performance and field degradation. It describes some of the limitations of superabsorbent polymer chemistry and some of the challenges to filter monitor performance. The API and Energy Institute (EI)

published a revision of API/IP 1583 (4th edition) in September 2004 to clearly communicate inherent limitations in filter monitor performance and clarify the responsibilities of vendors and users in the proper application of this technology. Further, the API and EI are developing the most extensive revision of API/IP 1583 to date, the 5th edition, to mandate an improvement in the performance of filter monitors. This paper discusses these revisions in some detail with a focus on the rationale for strategic changes. The development of new or modified performance tests, as related to superabsorbent polymer limitations or handling/distribution system stresses, is described.

EXPERIENCE WITH THE USE OF A PARTICLE COUNTER IN MEASURING FUEL CONTAMINANTS

Anthony Kitson-Smith, Peter Brook, Garry Rickard, Matt Fielder, Shaun Skilton, Steve Dickens, Vic Hughes

Within the aviation industry there are growing concerns with “critical contaminants”. Fine particulate is the cause of wear in mechanical devices (pumps, valves, meters etc.) but to be able to set quantitative limits for them will require the establishment of new detection methods to replace current subjective or ones that are deficient in some way in terms of the analytical challenges¹. Results of work using a Parker Hannifin CM20 laser instrument were presented in which good correlations were obtained with more traditional detection methods such as visual testing (Clear & Bright) and filtration time whilst gravimetric methods were shown to be erratic both in laboratory and field applications². In this paper the authors present an update on this ongoing project to develop a non-subjective quantitative method for the determination of contaminant levels in aviation turbine fuels. Recent activities include the launch of a new instrument design specific for aviation use, lodging of a new Energy Institute Test Method (to become an ASTM method in due course), the initiation of dialogue with engine OEMs to set operational limits and finally further R&D into methods to rapidly differentiate between different types of contaminants.

SESSION 11: AVIATION FUELS

AVIATION FUEL VOLATILITY – A BRIEF HISTORY

Kurt H. Strauss

The paper traces the historical changes in both aviation gasoline and aviation turbine fuel volatility from inception to the present. Specification developments over the years are noted and typical test results are cited. The effects of major volatility parameters are explored for both fuel types as is the relationship between fuel quality and aircraft/engine performance. Changes in volatility due to handling and storage are discussed. Test method limitations are pointed out. The impact on availability is also considered.

THE JOINT BATTLEFIELD USE FUEL OF THE FUTURE (J-BUFF) PROGRAM – CLEAN AVIATION TURBINE FUELS FOR THE U.S. MILITARY

William E. Harrison III, Patsy Muzzell and Leo L. Stavinoha

The Office of the Deputy Under Secretary of Defense, Advanced Systems and Concepts, has established a Clean Fuels Initiative with the intent to catalyze commercial industry to produce clean aviation turbine fuels for the U.S. Military from secure domestic resources. As part of this initiative, the Joint Battlefield Use Fuel of the Future Program, or simply J-BUFF Program, encompasses the activities required to evaluate, demonstrate, certify and implement the clean aviation turbine fuels that will be produced. The use of clean aviation turbine fuels in military tactical vehicles, aircraft and ships will reduce DoD dependence on foreign oil, reduce DoD supply chain vulnerabilities, and reduce DoD pollutant emissions. Evaluations of Fischer-Tropsch (FT) fuels, one type of clean fuel falling under the OSD Clean Fuel Initiative, are being conducted by a Joint Agency DoD-DoE fuels lab team. Results from these evaluations have shown FT fuels, if properly additized, to be good candidates for use by the U.S. Military. Initial implementation of FT fuels in military fleets will be accomplished with blends of FT fuel and petroleum fuel.

FUELS EFFECTS ON PARTICULATE AND GASEOUS EMISSIONS MEASURED IN A T700 TURBO-SHAFT ENGINE

Richard A. Kamin, Sherry A. Williams, Paul Penko, Clifford Moses

Numerous US Navy and Marine Corps air stations are located within EPA-designated air quality nonattainment areas. Aircraft emissions are a significant contributor to the total emissions generated by an air station. In 2003, the US Navy undertook a study to compare and rank particulate and gaseous emissions of various fuels, ranging from very clean synthetic fuels to high sulfur diesel fuels. Two synthetic fuels, one containing zero sulfur and zero aromatics and a second containing zero sulfur and 14 vol% aromatics were tested as potential future Naval fuels. A military specification JP-5 aviation fuel, typical of fuel being used today, was also included as a baseline fuel. This JP-5 was tested by blending with an aromatic solvent to increase the aromatics level and provide data on the effect of aromatics on emissions. The JP-5 fuel was also contaminated with copper to simulate the shipboard environment where copper leaches into the aviation fuel through copper-nickel piping contained in the fuel distribution system. A diesel fuel meeting the requirements for military specification F-76, containing 0.46 wt% sulfur, was also included as a comparison fuel. In addition, four of the fuels (JP-5, JP-5 with increased aromatics, JP-5 contaminated with copper, and F-76) were evaluated with and without the GE-Betz +100 thermal stability improver additive, to determine any impacts the additive may have on particulate emissions. Emission measurements were made in the exhaust of a T700-GE-700 helicopter turbo-shaft engine, mounted in a fixed test stand. Measurements of particle size and distribution were collected as well as gaseous measurements for: NO, NO_x, CO, CO₂, and UHC. Data from this project will be used to compare and rank the emissions of current and potential future Naval fuels, to provide additional information on how fuel characteristics play a role in aircraft emissions, and to potentially provide information that would assist in lowering aircraft emissions for those bases located in nonattainment areas. The intent of this paper is to provide a comparison of the gaseous and particulate emissions by fuel type.

“ARABIAN JET A-1 PLUS”, ENHANCING THE SAFETY, CLEANLINESS QUALITY AND THE ENVIRONMENT OF JET FUELS IN THE MIDDLE EAST

Ubaidallah S. ALGHAMDI

This presentation will provide an overview of the “Arabian Jet A-1 Plus”, which was a result of the Dhahran-Dubai 2003 Proactive Initiative to Enhance the Safety, Cleanliness Quality and the Environment of Jet Fuels in the Middle East. The initiative was announced by the Arabian Fuels Technology Center, in a press conference during the Dubai 2003 Air Show. The document defines the specific type of "Arabian Jet A-1 Plus" properties and test requirements for Aviation Turbine Fuel for civil use. The “Arabian Jet A-1 Plus” requirements meet or exceed the most stringent “Jet A-1” requirements of the latest editions of the following International Specifications and Guidelines: ASTM D 1655, UK DEF STAN 91-91, IATA Guidance Material GM and the AFQRJOS Check List with slightly higher performance. The main features are the higher flash point (45 Deg C Min.), lower contents of; sulfur, water, gum, and particulates matters. Also the requirements for Management of Change and Micro-Organism Detection & Control Awareness Programs are needed. It should be stressed that the "Arabian Jet A-1 Plus" Standard, Issue # AFIG-181203 was developed in harmony with the above International Specifications and Guidelines, the same approved test methods, additives, detailed requirements and procedures are utilized. The standard also addresses Specific Climatic and Operational Challenging Conditions in the Middle East Region. Revisions of the "Arabian Jet A-1 Plus" will be closely coordinated with ASTM D02.J, IATA AFWG, UK Aviation Fuels Committee and the concerned Regional Organizations in the Middle East through the Aviation Fuels International Group (AFIG) Chairman, under the umbrella of the Arabian Fuels Technology.

POSTER SESSION

EFFECTS OF AROMATIC AND SULFUR CONCENTRATION IN JET FUEL ON EMISSIONS OF A T63 ENGINE

Orvin R. Monroig, Edwin Corporan, Matthew J. DeWitt, Ben Mortimer, David Ostdiek, and Matt Wagner

This study consists on comparing the emissions from a T63 engine operated with jet fuels containing different aromatic and sulfur concentrations. A natural gas derived synthetic jet fuel (synjet) was used as the baseline fuel for this investigation. Synjet provided an aromatic/sulfur- free jet fuel with similar chemical characteristics (hydrocarbon range) as Jet A-1 or JP-8. For the aromatics, a blend of three different aromatic solvents was used to simulate the aromatic components in a typical jet fuel. Tert-Butyl Disulfide was used to increase the sulfur content in the fuel. The jet fuel aromatic/sulfur content was varied independently using on-line high precision syringe pumps. The engine was operated at two power settings to study the effects of aromatics and sulfur at different engine conditions. The particulate emissions were characterized primarily using commercially-available instrumentation to measure particle concentration, size distribution and particulate mass emissions. PM samples were collected for off-line analysis to obtain information about the effect of the aromatics and sulfur on the polycyclic aromatic hydrocarbon (PAH) content and carbon composition of the particles. In addition, gaseous emissions were primarily quantified using a Fourier transform

infrared (FTIR) analyzer. Test procedures, analysis techniques, and results will be presented.

THE COMBINED EFFECTS OF STATIC DISSIPATOR ADDITIVE AND FUEL IMPURITIES ON THE SEPARATION OF WATER FROM AVIATION FUEL

Janice I Hetherington and Lyndsay Copson

It is well documented that the microseparometer rating of an aviation fuel may be reduced by the addition of the static dissipator additive Stadis 450. Stadis 450 is added to increase the conductivity of the fuel but the magnitude of the conductivity response is known to be sensitive to polar contaminants and phenolic impurities in the fuel. This work investigates the combined effects of these same impurities and Stadis 450 on the microseparometer rating of a model aviation fuel. The results suggest that the microseparometer rating of a fuel containing Stadis 450 is also affected by the impurities in the fuel and that the values may be higher in the presence of phenolic impurities and lower for impurities such as naphthenates. This has important implications for the interpretation of microseparometer ratings and could explain the apparent variability in results from the test.

LABORATORY ASSESSMENT OF A NOVEL JFTOT TUBE RATING TECHNIQUE

Peter S. Brook, QinetiQ and Michael Croudace

USE OF A PARTICLE COUNTER TO MEASURE WATER DROPLET AND PARTICLE SIZE IN AN IDEAL FUEL.

Peter S. Brook and Garry K Rickard

Both dirt and water in fuel distribution systems are mobilised by surfactants. Despite numerous efforts over the past few years no simple, quick field technique has emerged to identify fuels which have levels of surfactants that may cause operational problems. The work undertaken at QinetiQ shows the use of a particle counter to measure water droplet size and distribution in simple dodecane, AOT, water mixtures. Petronate L and AOT have also been used to investigate the effects of surfactants on particle agglomeration in dodecane. The initial results suggest that a particle counter may be able to predict/identify problematic fuels.

PREPARATION AND CHARACTERIZATION OF BOURI VACUUM RESIDUE DERIVED PITCHES BY AIR BLOWING

H. A. El-Akrami and A. B. Shebli

In this study, Bouri crude oil has been selected as a raw material to prepare pitch precursors for carbon fiber production by air blowing. Bouri vacuum residue with a softening point around 60 C was air blown at 250, 275, and 300 C, respectively, for various periods in order to prepare a qualified precursor. The chemical changes which occurred due to air blowing has been studied by various characterization techniques such as elemental analysis, solubility measurements, thermogravimetric analysis (TGA and DTG), softening point (SP), and

infrared spectroscopy (IR). Results show that air blown markedly increased the softening point according to the severity of the conditions. The formation of the oxygenated compounds was the major feature of the air blowing technique. The softening of the blown pitches could be raised to about 210°C, giving a yield of 68%. IR analysis of the air blowing pitches showed that the relative intensities of the bands associated with the aliphatic structure decreased with increased softening point, while the bands of the aromatic structure were found to be slightly increased. Also the coke yields of blown pitches, determined by thermogravimetric analysis (TGA), increased as softening point increased.

B-JET PROJECT: CRYSTALLIZATION OF FATTY ACID METHYL ESTERS USING A SCRAPED SURFACE HEAT EXCHANGER – MONITORED BY FOCUS BEAM REFLECTANCE AND PARTICLE VISION MEASUREMENT PROBES

Michel J. Delafontaine, Robert O. Dunn and C.R. Krishna

Extension of jet fuel with biofuels is a viable alternative to the development of totally new fuel types. Developing a renewable fuel that does not require major alterations on the current aircraft fleet will have a direct impact on our current dependency issues. A portfolio of such products is being investigated as potential extenders of jet fuel. They are derivatives from vegetable oil and one of them is already used in ground transportation (Biodiesel) in blends with diesel fuel. Biodiesel has been tested successfully in aviation jet turbine and has shown improvement in emissions.

B-JET PROJECT: PERFORMANCE AND EMISSION TESTING RESULTS

Maxwell E. Shauck, Grazia Zanin and Sergio Alvarez

The problem with Biodiesel is the high cloud point (CP) due to the presence, mostly, of saturated fatty acid methyl esters (FAME). Removing these components can be done through fractional crystallization. A successful fractional crystallization of Biodiesel depends on the production of slurry containing crystals that can be separated from the liquid phase with maximal yield. Growing large crystals of FAME in a relatively short time was the object of this research. This was achieved using a tubular scraped surface heat exchanger. The crystal size and distribution were analyzed *in situ* by Focus Beam Reflectance Measurements (FBRM). An *in-process* video microscope provided real time *in situ* visualization of the crystals. While the CP and the Pour Point (PP) of the FAME were determined by the ASTM methods at around 2°C, it had to be cooled below -3°C to obtain consistent slurry of crystals in suspension. It appears that the FAME was to be cooled to supersaturation in the metastable zone to induce nucleation. The constant scraping of the heat exchange surface allowed the efficient transfer and a retention time of less than one hour to go from a temperature of 15°C to -3°C, where a steady state of crystallization was obtained. Although the slurry was cooled below the PP, it was flowing freely from the heat exchanger. When the slurry was warmed up slowly, a clear shift of the mean size distribution from the smaller to the larger crystals was observed. The low retention time and the potential multi-step nucleation technique using scraped surface exchangers are discussed.

EVALUATION OF BOTD AS LUBRICITY EVALUATOR FOR CI/LI IN SYNTHETIC JP- 8/JP-5

Leo L. Stavinoha, Patsy A. Muzzell, Brian McKay, and Luis Villahermosa

Synthetic hydrocarbon fuels are being developed as an alternative to petroleum-derived fuels to reduce dependence on imported petroleum crude oil and can be used to meet Energy Policy Act (EPACT) alternative fuel requirements. These fuels, which contain essentially zero sulfur and no aromatic hydrocarbons, comply with more stringent Environmental Protection Agency (EPA) clean fuel regulations and are produced from natural gas, coal or biomass using Gas-to-Liquids (GTL) technology employing Fischer-Tropsch (F-T) catalysis. However, synthetic fuel does not possess the natural lubricating qualities associated with conventional diesel fuel. Lubricity additives will be needed to eliminate poor lubricity fuel that would increase engine fuel pump and injector wear-induced premature pump failure and poor performance. The objective of this research was to determine the sensitivity of the Ball On Three Disks (BOTD) bench-top lubricity tester to military fuel corrosion inhibitor/lubricity improver (CI/LI) additive used in poor lubricity synthetic aviation turbine fuel. The amount of additive concentration required to prevent excessive engine fuel pump and injector wear has been quantified and the BOTD has been shown to have correlative utilization over other diesel fuel lubricity bench-top tests including the Scuffing Load Ball on Cylinder Lubricity Evaluator (SLBOCLE) and High Frequency Reciprocating Rig (HFRR). The BOTD compares favorably with the lubricity additive qualification bench-top test (Ball on Cylinder Lubricity Evaluator [BOCLE]) because of its lubricity additive sensitivity; however, published data indicates that it can more adequately represent conditions found in fuel pumps. Lubricity improver additive, at minimum and maximum treat concentrations, were blended with a synthetic JP-5 hydrocarbon fuel containing no sulfur or aromatic species. The blends were then tested using the BOTD to determine their respective wear scars. Wear was determined to decrease as the lubricity additive concentration increased in a non-linear fashion. This data, along with future test development, has the promise of leading to a lubricity bench-top test that can reliably determine the lubricity of military fuels containing CI/LI additive and support a minimum additization specification for synthetic fuels. Military turbine fuel (JP-8 and JP-5) requires the addition of CI/LI that is effective in reducing unacceptable wear in arctic designed rotary fuel pumps used in HMMVV vehicle diesel engines. These lubricity additives were previously not detectable in fuel using industry developed diesel bench-top lubricity tests. The BOTD has been shown to be sensitive to CI/LI-additized, poor lubricity synthetic JP-5 fuel. This lubricity bench test can be pursued for development into a standard test for use in fuel specifications. This technology may also be useful in developing specifications for use of other commercial lubricity additives that could than be introduced into military fuels.

CURRENT DEVELOPMENTS IN JFTOT PERFORMANCE

George R. Wilson, III and Philip Fruin

A recent survey of participants in the ASTM ILCP introduced concerns that the method was not being performed in the most optimum manner. As a result of this the authors started a series of tests to examine the performance effects of running the JFTOT test in the range of conditions allowed by the method and those the survey suggested were common to actual practice. As a result of this the authors have developed significant information on how the

test needs to be conducted to optimize performance and how to achieve that goal.

INTEGRATING A FIELD MOBILE LAB FOR FUEL ANALYSIS – ENABLING THE PQAS

George R. Wilson, III, James Doherty, Scott Hutzler, and Larry Smith

The US Army needs fuel quality and conformance information closer to the front than can be provided by current quality control practices. Correct analysis of fuel quality and cleanliness can have direct impact on unit readiness. Pushing the analysis capability beyond Clear and Bright is the mission of the Portable Quality Assurance System, the PQAS. The first priority of the Army was to pare down the available tests to a workable number. Using MIL-STD-3004 as a guide they streamlined the test requirements to those that would give the most pertinent information. Having chosen the tests and ordered the equipment they were still faced with the question of how to make the system work. The soldier running the PQAS will be well trained in test procedures but will not be a fuels expert. They will not know explicitly what to run on each sample nor will they have time to page through the standard to make that determination. To make the PQAS effective it needs a well designed, interconnected software system to direct the actions of the users. The authors were tasked with generating the integrated operating system for the PQAS. The three main goals were: 1) Simple to operate; 2) Compliant with MIL-STD-3004; and 3) Transparent databasing for data analysis. The journey to completion covered areas as mundane as how to page between samples being tested to those as esoteric as information as a logistic commodity. The integration has been successful and the PQAS has been deployed. The PQAS can stand as a model approach for other applications for field testing.