7TH INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS
Graz, Austria
September 24-29, 2000

Abstract Summaries

SESSION 1: DIESEL FUEL STABILITY

THERMAL STABILITY OF DIESEL FUEL
Scott D. Schwab, Timothy J. Henly, Joel F. Moxley and Keith T. Miller.

The recent trend toward higher operating temperatures and pressures in advanced diesel fuel systems has resulted in greater thermal stress on diesel fuels. Consequently, there is an increased concern about the thermal stability of diesel fuel. Several tests have been developed to assess the thermal stability of distillate fuels. One test that has been historically used is the “Pad” test, ASTM D6468. In this test, the presence of cetane number improver additive, 2-ethylhexyl nitrate (EHN), accelerates the formation of sediment in some fuels. Since this additive is widely used to both improve diesel fuel performance and reduce emissions, a study was carried out to determine if EHN could decompose and cause either filter plugging or injector fouling in a modern heavy-duty diesel engine. Measured fuel temperatures and residence times within a 1998 Cummins M-11 engine operating under severe thermal conditions were far removed from the conditions used in D6468. A fuel with 5000 ppm added EHN that was unstable at D6468 aging conditions showed no tendency to form sediment or deposits when run in the M-11 engine. No correlation was found between a fuel’s D6468 performance and the formation of injector deposits in the L-10 test. A laboratory scale filtration test was developed and used to determine the thermal conditions required to cause enough fuel degradation to significantly restrict flow through a fuel filter. Determination of the decomposition rate of EHN at various temperatures indicated that breakdown of EHN is negligible at even the most severe engine fuel conditions. These observations indicate that no problems associated with the use of EHN-treated fuels should be expected in modern heavy-duty diesel engines.

DIESEL FUEL STABILITY AND INSTABILITY: A SIMPLE CONCEPTUAL MODEL
John D. Bacha and Andrea N. Tiedemann

Identifying the root cause of an incident of inadequate diesel fuel stability is usually complicated by the myriad of possible contributing factors. The process can be simplified, however, by use of a simple experience-based model that organizes contributing factors into sets of principal and subordinate factors. Experience teaches that the insoluble matter that is the product of fuel instability results from the confluence of precursors, conditions, and moderating factors. One or more subordinate elements of these principal factors can fully explain conversion of precursors to deleterious insoluble matter. Examples demonstrate application of the conceptual model.

150°C DIESEL STABILITY TEST (ASTM D 6468): A VERSATILE LABORATORY TOOL

John D. Bacha and Cyrus P. Henry Jr.

The Octel F21-61 Accelerated Fuel Oil Stability Test and variants thereof have been used by fuel technologists for more than 50 years, for rapid assessment of diesel fuel stability. A standardized version of the 150°C test method was recently adopted by ASTM as Test Method D 6468, Standard Test Method for High Temperature Stability of Distillate Fuels. A number of features distinguish the standardized test method from its predecessors. Examples demonstrate the utility, versatility and value of the test method as a rapid stability assessment tool.

THE SEARCH FOR THE HOLY GRAIL: A FAST, PORTABLE WAY TO DETERMINE THE INHERENT STABILITY OF MIDDLE DISTILLATE FUELS

Mike Sherratt

A review of different ways to determine the inherent stability of middle distillate fuels shows that test times can vary from a few weeks for test temperatures just above ambient to a few hours at higher temperatures. Results of these tests show levels of precision which make their use in specifications difficult and correlation between different methods is not always evident due to the complex chemical reactions that take place at these elevated temperatures. Research has led to a new spectrophotometric method which takes just 30 minutes at ambient temperature to give a result which has been shown to correlate with existing tests. Further work has resulted in the development of a portable instrument and its subsequent inclusion in a military diesel specification. Analysis of test results will show if the Holy Grail has been found.

SESSION 2: USE OF ADDITIVES IN DIESEL FUEL & HEATING OIL

ADDITIVES FOR STABILIZATION OF LOW-SULFUR DIESEL CONTAINING 2-ETHYL HEXYL NITRATE CETANE IMPROVER

Cyrus P. Henry Jr. and Neva E. Montgomery

It has been known for many years that 2-ethylhexyl nitrate (2-EHN), the most commonly used cetane improver additive for diesel fuel, can degrade the thermal stability of diesel fuels in some accelerated stability tests, particularly tests carried out at temperatures exceeding the auto-decomposition temperature for the additive. As reported earlier by Bacha and Lesnini 1 the Octel F21 150°C test can be used to evaluate fuel sensitivity to 2-EHN. This effect is fuel dependent and is observed for both high and low sulfur diesel fuels. Additives have been developed that effectively counter instability due to addition of 2-EHN.

LUBRICITY PROPERTIES OF DIESEL FUELS AND THEIR IMPROVEMENTS BY USING LUBRICITY ADDITIVES

Christian Bernasconi, Franck Eydoux and Laurent Germanaud.

The lubricity of Diesel fuels must be sufficient in order to avoid high pressure injector pump failure. Low sulfur Diesel fuels often exhibit poor lubricity properties, since many of them are obtained by deep hydrotreatment that eliminates most of the polar compounds previously contained in the fuels and responsible for their original good lubricity. A suitable Diesel fuel lubricity has been established in Europe by using the HFRR method (ISO 12156-1 standard): the HFRR wear scar diameter (WSD) obtained after testing a Diesel fuel must be lower than 460 µm to ensure that this fuel has sufficient lubricity. When necessary, better lubricity can be restored easily by using additives. However, these additives must not only have good physical and chemical stability alone or after incorporation in multifunctional formulations, they must also be fully compatible with other additives that may be present in the fuel such as flow improvers (FI), wax antisettling additives (WASA), detergents, etc., with engine lubricants and with materials such as elastomers used in engines and fuel handling equipment. To verify this physical and chemical compatibility, and ensure that each additive maintains its full efficiency after being mixed with others in multifunctional formulations or in the fuel itself, several « no-harm » tests have been carried out on additive formulations or additized fuels. This paper reports experimental results on the above, and demonstrates that suitable lubricity improvers can be widely used to improve the lubricity properties of low sulfur Diesel fuels and that, furthermore, no negative interactions between additives, additized fuels and lubricants have been detected.

IMPROVEMENT OF THERMAL STABILITY OF DIESEL FUEL USING TERTIARY ALKYL PRIMARY AMINES

Rajiv Banavali and Bharati Chheda

To address the emission reductions, engine manufactures are fabricating more stringent engine designs that will impact fuel performance and stability. Diesel fuel temperatures and pressures are expected to increase significantly when systems such as exhaust gas recirculation and common rail systems are introduced. The recirculating fuel returning to the fuel tank from the cylinder head will be much hotter, putting further strain on the oxidation stability of the fuel. Thermally unstable fuel can cause environmental problems, lower the fuel economy, and form deposits that can steadily deteriorate engine performance. Nozzle deposits and gumming on control valves at high temperatures are reported to reduce peak engine performance. Engine filter plugging in some fuels with cetane improvers has been correlated to poor thermal stability at 150° C. Therefore, there is a need for additives that can help fuel withstand higher temperature and pressure without any degradation that causes gum and sediment formation. Our work to study the thermal stability of the diesel fuel utilizing Tertiary Alkyl Primary Amines (TAPA) has led us to believe that TAPA can help in improving the thermal stability of the fuel. Moreover, this can be done with synergistic benefits. We have investigated the thermal stability of a variety of diesel fuels, with and without light cycle oil and organic nitrate added. We have compared the performance of TAPA with the known additives used in diesel fuel. In this paper we will also report our mechanistic investigation into the chemical details of the stabilization. Effect of the

TAPA chemical structure on the diesel fuel stability is correlated with pathways preventing gum and sediment formation.

THERMAL STABILITY IMPROVEMENT IN DIESEL FUEL BY ADDITIVES

Paul Yon-Hin and John D. Bacha

Among a number of quality requirements for diesel fuel, thermal stability is an important property. Poor thermal stability, as measured by the popular 150°C laboratory test method (ASTM D 6468), is usually associated with premature fuel filter plugging by diesel fuel end-users. Thermal stability behavior of a high sulfur diesel fuel and its three components was studied with a view to maximize the thermal stability of the high sulfur diesel fuel. It was found that combining components with reasonably good thermal stability could produce a high sulfur fuel with poor thermal stability. The results also showed that the 150°C test method when run for 180 minutes instead of the usual 90 minutes can differentiate between fuels with good or poor thermal stability. In this study, it was also found that traditional additives normally called stabilizers with acids neutralizing properties were not always successful in providing or improving the thermal stability, especially when the 150°C test was run for 180 minutes. It was concluded that additives having both acids neutralizing and dispersing properties are more effective in improving the thermal stability of high sulfur diesel fuel.

STABILITY IMPROVEMENT OF LIGHT HEATING OIL

Gabriele Lohmann, Hubert Jungbluth, Gary Bailey

Multipurpose additives offering a combination of different additive effects are a reliable and economic mean of improving the specification of Light Heating Oil. The ageing of middle distillates (light heating oil) depends on a combination of different factors such as crude oil quality, refinery processing and storage conditions. For this reason no single component additive (mono compound additive) is able to give sufficient control of ageing for all commercially available middle distillates.

SESSION 3: MIDDLE DISTILLATE FUELS

IT AIN'T SO SIMPLE: A STUDY OF VARIABLES AFFECTING THE PURITY OF MIDDLE DISTILLATE FUELS DELIVERED FROM A STORAGE TANK

Edmund W. White

The results of an accelerated stability test do not indicate by themselves the rate of contamination build-up in a fuel in a storage tank. The accelerated test is only a measure of the inherent stability of the fuel under laboratory controlled conditions. It does not incorporate considerations of microbial contamination, of windblown particulates, of the environment in which the storage tank exists, of tank design factors, of local housekeeping and operational policies, or of incompatibilities among various fuel lots that are introduced into the tank.

This paper reviews existing knowledge on a number of these multitudinous factors. It examines several theories concerning the chemistry of incompatibility, some microbial growth factors, interactions of the fuel system with the environment, and the design, maintenance, and operational needs.

COMPATIBILITY AND EFFICACY OF SELECTED DIESEL FUEL BIOCIDES
Steven R. Westbrook

This paper presents the results of a project to determine the relative compatibility and efficacy of three diesel fuel biocides. The interaction of these biocides with diethylene glycol monomethyl ether (fuel system icing inhibitor additive) was also investigated. Each of the biocides was evaluated using standard microbiological techniques to determine additive efficacy and compatibility with other fuel additives. The relative effectiveness of the biocides was determined. The military's aviation kerosene, JP-8, also contains an icing inhibitor additive that has some biocidal activity. This study was conducted to evaluate the efficacy of the individual biocides as well as the possible interactions (either synergistic or antagonistic) between these biocides and the icing inhibitor additive.

A NEW TECHNOLOGY FOR REMOVING NITROGEN-CONTAINING COMPOUNDS FROM MIDDLE DISTILLATES
Whasik Min, Shinyoung Khang, Jaewook Ryu, Kwansik Yoo, Seungwoo Lee, and Cheoljoong Kim

SK corporation of Korea has developed a new process to produce ultra-low-sulfur-diesel by improving the activity of hydrodesulfurization catalyst by removing small traces of nitrogen-containing compounds from HDS feedstock. The experiments have revealed that the degree of improvement in hydrodesulfurization is essentially proportional to the removal ratio of nitrogen-containing compounds. For middle distillate feedstocks, for example, 90% removal of nitrogen-containing compounds, resulted in roughly the same percentage of gain in product sulfur level enhancement. SK corporation has built fairly large data sets by performing numerous pilot tests. Based on such data, a new process for economical and efficient removal of nitrogen-containing compounds is under development. The storage stability of nitrogen-removed-then-hydrodesulfurized diesel product has also been investigated. While the solely HDS treated material exhibited gradual color darkening, the nitrogen-removed-plus-hydrodesulfurized showed good color stability maintaining its bright color. Pretreated plus HDS material shows at least a 1 ASTM color improvement over the material that is HDS treated only.

SESSION 4: FUEL PRODUCTION, ANALYSIS, AND TRANSPORTATION

DEVELOPMENTS IN FUEL OIL BLENDING

Frans G.A. van den Berg

Residual Fuel Oil continues to be one of the main refinery products, constituting about 18 % of the average product barrel. Overall world demand is expected to increase slowly, in spite of environmental pressures. The RFO scene is impacted by a number of developments, notably the replacement of inland fuel by natural gas, the increasing use of low sulfur (more paraffinic) and other novel crudes and the trend towards more severe operation of refinery conversion units. In addition, the present economic climate forces the refinery to reduce costs and minimize quality give-away on relevant properties such as viscosity. The present trends are expected to cause a further decrease in the "stability reserve", the capacity to keep the asphaltenes in solution, of the global residual fuel oil pool and increases the likelihood of fuels becoming unstable, leading to significant costs for refineries, marketeers and end-users. This requires improved methods and guidelines for the control of RFO stability. Shell companies use a number of tools to measure fuel oil stability; a survey of the present methods is given in this paper.

STABILITY AND COMPATIBILITY OF PARTIALLY UPGRADED BITUMEN FOR PIPELINE TRANSPORTATION

Parviz M. Rahimi, Richard J. Parker, Ritchie Knoblauch, and Irwin A Wiehe

Pipeline transportation of Athabasca bitumen was investigated using a combination of diluent and a mild thermal reaction. A model was developed to predict the amount of diluent required for Athabasca bitumen to meet pipeline viscosity specification (350 cP). Good agreement between predictive and measured viscosities was obtained when this model was applied to visbroken products. The amount of diluent was reduced to as low as 6 vol% when Athabasca bitumen was treated thermally at relatively mild conditions. Stability of the visbroken products was determined using P-value and solubility numbers. The results indicate that, under the severity employed, the products were relatively stable even after two years. Using solubility numbers for visbroken products, it is possible to predict the severity at which instability will occur because of coke formation.

USE OF THE PORLA AUTOMATIC HEAVY FUEL STABILITY ANALYSER FOR THE MONITORING OF H-OIL PLANTS

Juha Vilhunen, Alain Quignard Alain Quignard, Olli Pilviö and Jürg Waldvogel

The H-Oil process is a commercial ebullated-bed licensed by IFP. It is used to convert typically 50 to 75 percent of the vacuum residue in the feedstock into distillates. The production of a stable, high quality heavy fuel oil with a high conversion level is a difficult challenge. The stability (Flocculation Ratio FR) and the compatibility (Peptising state of asphaltenes P-Value) of residual H-Oil fuels are the key parameters. The analytical test is based on the addition of a paraffinic solvent (iso-octane) to heavy oil / aromatic solvent (xylene) mixtures of variable

proportion until asphaltenes precipitate. FR and P-Value are calculated from the consumption of iso-octane at the flocculation. A simplified method used for the monitoring of pilot plants is based on the measuring of FR at a given solvent (aromatic/paraffinic) to oil ratio, typically 5/1.
The new generation PORLA analyser by FMS is a powerful and reliable laboratory instrument to determinate both, stability and compatibility parameters. The new measurement software has been developed in collaboration between IFP and FMS. When compared to the manual method, PORLA results have been shown to be in very good agreement on FR and P-value. Correlations developed by IFP on an extended range of H-Oil residua are shown in this paper. It has been proven to be very useful for the monitoring of pilot plants and for comprehensive studies of feedstock effect, catalyst effect or operating conditions effect, with regards to conversion level and stability. Examples are given in this paper. The PORLA Analyser gives accurate results with a repeatability 3 times better than by the manual method. It enables to run the process very near to the operational limits for a pilot or an industrial plant. It is easy to use and the laboratory operator time is shortened very significantly. This user-friendly analyser can be also used by process operators.

USE OF ON-LINE PETROLEUM TEST EQUIPMENT FOR ENHANCED QUALITY OVERSIGHT AND SAMPLING OF PRODUCTS TRANSPORTED BY AUTOMATED FUNGIBLE PIPE LINE

Kenneth Bailey, Henry A. Burmeister, IV, Eric A. Gustafson, and Gretchen A. Wendtland

Quality oversight to detect contamination of petroleum products is a critical component of operating a fungible pipeline system. In the pipeline industry, the recent trend has been toward automation of pipeline operations through real-time communication to a central supervisory control and data acquisition (SCADA) system. SCADA systems allow pipeline controllers to monitor fluid stream properties, operate pumps and valves, and react to system and product anomalies. In conjunction with a SCADA system, on-line test equipment for key properties, such as API gravity (density), haze, and flash point allows continuous monitoring of products for contamination, real-time alarms, trending, and allows immediate reaction to quality problems. Batch quality profiles from on-line test equipment are critical for determining cut points between batches of different products. Sophisticated multi-batch sampling systems enhance quality control through composite sampling. This paper is a case analysis of the use and benefits of on-line test equipment for automated product quality control, product deliveries, and composite sampling by Buckeye Pipe Line Company.

SESSION 5: LONG-TERM & STRATEGIC STORAGE

DETAILS OF THE ISPG PREDICTION SYSTEM FOR ABOVEGROUND STEEL TANKAGE

Jun Shigeta, J.W. Joachim Koenig, and Hiroaki Maruyama

Since 1998, Japan National Oil Corporation(JNOC) has developed Crude Oil Sludge Prediction System for aboveground tank as the experimental center of International Sludge Project Group. JNOC has many sludge accumulation data and experience on crude sludge operations at the stockpiling bases. However JNOC has not been able to clearly find out crude sludge phenomenon and has controlled crude sludge only by experimental operation. Through the development of Prediction System co-ordinated by Dr. Koenig, many original variables of sludge phenomenon have been studied and discussed. Now we have come to reach our solution using decision tree and risk analysis like EQPS of petroleum products.

PREVENTION OF WAX FALL-OUT DURING LONG-TERM STOCKPILING OF CRUDE OIL

Takao Hara, Hiroaki Maruyama, Shuichi Isida, Masataka Kawai, Kiyomasa Shinbori and Yoshihiko Kon

Organic sludge deposited during long-term stockpiling of crude oil reserved by Japan National Oil Corporation is exclusively waxy sludge and is to be composed of crystalline n-paraffins of substantially higher carbon numbers existing in the W/O type oil-water emulsion (T. Hara, 6th IASH, 1997). In the present study, the possibility for prevention of wax fall-out during storage of crude oil through the solute-solvent interaction is proposed. A commercial paraffin wax (carbon number distribution: C 23~47) was added to 8 kinds of Middle East crude having wide density range of 0.8258-0.8867 g/cm3 at 15 ℃. Maximum soluble wax content and distribution of carbon number among n-paraffins were measured in the temperature range of 10~45 ℃. Saturate amounts of wax, particularly that of higher carbon numbers (C +28) were quite different among crude tested and were found to be highly estimated by the regression equation (variables: temperature, aniline point and density). The accelerated storage test for mixed crude composed of several combinations of two crude with temperature differential from 0 to 30 ℃ could demonstrate that wax fall-out was substantially reduced by the storage of certain combinations between two crude. The surplus dissolving ability for higher carbon-number wax of the particular crude may contribute the prevention of wax fall-out.

CONCENTRATION DIFFERENTIAL OF CRUDE OIL IN THE ABOVE GROUND TANK

Masataka Kawai, Hiroaki Maruyama, Shuichi Isida, Takao Hara, J. W. J. Koenig

Japan National Oil Corporation has managed the long-term crude oil stockpiling and their past investigation revealed the uneven settlement of the crude sludge in the above ground tank. (T. Hara, 6th IASH, 1997) Through the development of the crude sludge prediction system with International Sludge Project Group (ISPG), we presumed that the reason for the uneven settlement of crude sludge might be caused by concentration differential such as inorganic substances, water content, wax content, etc. We recently investigated horizontal and vertical condition of Zakum crude oil stored in the above ground tanks at MUTSU stockpiling base. Field examination clearly showed that viscosity and temperature varied horizontally as well as vertically. The multi layer samples were analyzed at NKKK laboratory and we found that density was almost constant excepting bottom layer sample. However, water contents and wax content of and C28 over varied horizontally as well as vertically. We concluded that concentration differential of water content and wax content played major role for the uneven settlement of crude sludge in the above ground tank.

SIMPLE METHOD FOR MEASUREMENT OF NUMBERS OF MICROORGANISMS IN THE LONG-TERM STOCKPILES OF CRUDE OIL

Kohtaro Kirimura, Hiroaki Maruyama, Yoshiharu Watanabe, Hironori Tatsuki, Hiroyuki Nakagawa, Ryuichiro Kurane, Kuniki Kino, and Shoji Usami

The numbers of microorganisms in the crude oil, stored in tanks for more than twenty years, were measured. For the measurement, the method based on the following two steps was utilized: (1) collection and enrichment of microorganisms by fractionation with isooctane and centrifugation, and (2) measurement of numbers of microorganisms stained with fluorescence dye (Hoechst 33258) under a fluorescence microscope. According to the method, the number of microorganisms was measured to be approximately 107~108 cells per kg in the crude oil, whereas it was approximately 108~109 cells per kg in waxy sludge. Since the numbers of microorganisms are generally of the order of 1011 cells per kg in soil, the numbers in the waxy sludge and crude oil are lower than those in the soil. However, in this study we found that numbers of microorganisms in the waxy sludge were greater than those in the crude oil itself. Therefore, there is some possibility that the microorganisms might have given some effects on the long-term stockpiles of crude oil, and that microorganisms might have directly or indirectly participated in sludge formation in the crude oil.

STUDIES ON THE CHEMICAL NATURE OF MALTENES SEPARATED FROM SLUDGE DEPOSITS

Latif H. Ali , Abdurazag A. Shebli, Marim K. Alnaed

A Viscous maltenic constituting about 70% of total sludge deposits weight of some stored Libyan crude oils was recently reported by us. The fractionations of this maltene by chromatographic and solvent extraction schemes were investigated in the present paper. A mere chromatographic fractionation on thermally activated alumina column gave 58% saturates, 14.9% aromatics and 9.5% polars. Alternatively, when the chromatographic fractionation was preceded by methyl ethyl ketone (MEK) isothermal solvent extraction, the operation yielded 24.1% wax, 76.0% oils and traces of asphaltenes (0.75%). The chromatographic fractionation of oils yielded 60% saturates, 20% aromatics and 11% polars; about 46%, 15% and 9% on original maltenes weight respectively. These data are discussed. Detailed spectroscopic investigation by 1HNMR, IR, UV and ultimate C, H, N analysis revealed interesting information and correlations with regard to the chemical nature of the fractions that were preliminary separated by column chromatography.

EXPERIENCE GAINED DURING THE FIRST YEAR OF USING EQPS AS A DECISION MAKING TOOL FOR MANAGEMENT OF LONG TERM STORAGE OF DISTILLATED FUELS IN ISRAEL

Yoav Armoni, Rafi Fass, Josefa Ben-Asher

There was almost no long-term storage of distillates in Israel until 1998. Storage tanks, which were defined as long-term storage, were actually used as open operative facilities. The distillates in storage were checked every 9 months. The list of tests performed on the fuel included

assessment of specification requirements and just one test for determination of long-term storage stability. Since the decision to "shut off" tanks and use the EQPS system as a tool for decision making, the following changes were made: 1) Exact requirements for tanks and terminals suitable for long term storage of jet fuel and diesel fuel were defined. 2) Procedures and intervals for drainage and cleaning of the storage tanks were specified. 3) New methods for evaluation of distillates quality in long term storage were implemented. These methods are not used in assessment of specification requirements. 4) It was decided to estimate the maintenance of the storage tanks by checking, at least once a year, the microbial growth at the tank bottom. Four tanks were found unsuitable for long term storage following the inspection. The tank owner was asked to upgrade them. Though most of the EQPS recommendations were acted upon some were overruled due to our conviction that the misleading recommendation from the quality prediction system was obtained due to incompatibility between the EQPS knowledge base and the infrastructure of fuel storage and distribution systems in Israel.

SESSION 6: FUELS FOR THE 21st CENTURY

ULTRA CLEAN FUELS FOR THE 21st CENTURY

David K. Olsen, F. Dexter Sutterfield and Arthur Hartstein

Clean air is fast becoming a world-wide problem. Vehicles currently accounting for a large portion of urban and regional air pollution, including carbon monoxide, nitrogen oxides, volatile organic compounds, and particulates. The transportation fuels market is demanding fuels that produce extremely low emissions. Clearly, oil must contribute the bulk of these fuels well into the next century. That challenge will require fuels that continue to change to answer the need for increasingly stringent emissions requirements. The United States Department of Energy (DOE) is conducting a program to develop new transportation fuels, engines, and exhaust catalysts to meet these needs. This paper describes DOE’s fuels effort. The DOE will create Government/Industry partnerships to perform research that enables petroleum-based fuels to meet new vehicle emission regulations; early emphasis will be on sulfur reduction in heavy crudes. This is important to oil producers and refiners. The lower-sulfur gasoline and, in particular, very low-sulfur diesel presents possibly insurmountable problems for current refining technology when the crude contains large amounts of sulfur, especially dibenzothiophenic sulfur. This difficulty in making low-sulfur products will likely cause the price differential between light, sweet crude and heavy crude to widen even further. Another focus of the program will be on the design, construction and operation of an innovative pre-commercial scale (e.g. 200 barrels per day) synthesis gas-based advanced fuel production facility. Because of the need for ultra low sulfur fuels (sulfur poisons the after-engine catalysts that remove other pollutants), the program is on a five-year fast track.

CHANGES IN JET FUEL – THE NEXT TEN YEARS?

Peter S. Brook, Garry K. Rickard, Jonathan O. Whitby

Jet fuel demand is increasing, requiring oil companies to employ innovative and alternative processes to maintain production levels to keep pace with demand. Fuels from non-conventional sources, such as synthetic and bio-fuels, are now emerging into the markets. Some likely effects of these products on gas turbine operation are considered. Current trends in jet fuel properties are reviewed and the possible influences on gas turbine engine operation associated with these changes are discussed. Some of the major driving forces behind changes to automotive fuel specifications in recent years have been legislative bodies concerned with possible environmental effects. These bodies may become a driving force for jet fuel change in the future. It is certain that the effect of changes to gasoline and diesel fuel specifications will feed through to jet fuel. The possible impact of these changes on jet fuel are discussed. Novel thermal stability additives offer an opportunity for equipment designers to take advantage of enhanced fuel thermal stability; these and other possible future developments in jet fuel additive technology are briefly discussed.

JP-900 FROM COAL LIQUIDS? THE USE OF DICYCLOHEXYLPHENYL-PHOSPHINE TO ENHANCE THE OXIDATIVE AND THERMAL STABILITY OF A MODEL COAL LIQUID

Bruce D. Beaver, Li Gao, Mitchel G. Fedak, Michael M. Coleman and Maria Sobkowiak

A model study is described that tests the feasibility of using organophosphorus compounds as additives to provide both oxidative and thermal stability for future coal derived jet fuels. The mechanism of autoxidation of selected organophosphorus compounds in model hydrocarbons at 150°C is examined.

FUEL STABILITY CHALLENGES IN A MARINE ENVIRONMENT: A US NAVY VIEW

Sherry A. Williams, Richard A. Kamin, Robert M. Giannini, and Dennis R. Hardy

Ship and aircraft propulsion fuels face unique stability challenges in the 21st century. Increasing hardware requirements, changing refinery practices, and stringent environmental mandates all contribute to these challenges. Unfortunately, the United States Navy (USN) is not immune to these issues. Having worldwide commitments to supply both ship and aircraft support, the USN is faced with difficult decisions regarding how to best address these stability issues in both ship and aviation fuels without compromising operational capability. What may be acceptable solutions for commercial ships, commercial aircraft, or land-based military aircraft may be unacceptable due to the USN operating environment. From long-term storage requirements; to the utilization of commercial distillate marine fuels; to the shipboard impact of the “+100” aviation fuel thermal stability improvers, the USN is constantly addressing stability problems and their potential solutions. The intent of this paper is to provide an overview, using current issues, of the USN philosophy, approach, and rationale to address the fuel stability challenges of the 21st century.

TECHNOLOGIES FOR MEETING LOW-SULFUR FUEL SPECIFICATIONS IN THE UNITED STATES
F. Dexter Sutterfield and David K. Olsen

Gasoline is expected to be the major transportation fuel in the United States for many years. Diesel fuel use is growing at a slightly faster rate than gasoline. High levels of sulfur in gasoline adversely affect the performance of catalytic converters used to reduce tailpipe emissions of CO, HC and NOx. The impact of sulfur seems more pronounced as emission standards become more stringent. Acceptable levels of sulfur in fuels are being debated in a worldwide forum. In late June 1998, the member states and the European Parliament agreed on key European fuel specifications for years 2000 and 2005. U.S. Tier 2 regulations require gasoline sulfur content to be 30 ppm average with an 80 ppm maximum. It is expected that emission control devices for NOx reduction for diesel engines will use catalysts that are adversely affected by sulfur. Light-duty diesel vehicles in the U.S. will have the same emissions targets as gasoline powered vehicles. The U.S. Environmental Protection Agency (EPA) has not issued diesel sulfur specifications at the time of this presentation, but it is expected that the sulfur content of on-road (highway) diesel will be lower (proposed 10 ppm average and 15 ppm maximum) than gasoline. Engine manufacturers are asking EPA to set the standard for sulfur in diesel below 10 ppm. Thus, it appears there will be ongoing attention to sulfur levels in fuels. Several technologies, in addition to conventional hydrotreating, have been developed for sulfur reduction in gasoline. These include pre-treating fluid-catalytically-cracked (FCC) feed and post treating of the FCC naphtha. Post treatment options include catalytic caustic extraction, solvent extraction, hydrotreating, catalytic distillation, and adsorption. Post-treatment processes have been developed for gasoline sulfur reduction that are efficient and fairly low cost. Significant capital investments must be made, and there is a loss of octane and/or volume that carries extra cost that is directly proportional to the amount of sulfur in the feedstock. Some of these processes have higher risk because they have not been proven in commercial experience. Unlike Europe, where the diesel comes from straight-run and hydrocracked stock, about one-third of the diesel in the U.S. comes from cracked (FCC and coker) stock. In the cracking process, sulfur compounds are made that are particularly difficult to remove by hydrodesulfurization. New processes may be developed in the future, such as bioprocessing, adsorption, or others, but hydrotreating technology will likely be the main or only process used to meet these reduced sulfur limits in diesel.

SESSION 7: BIODETERIORATION & MICROBIOLOGY

DETECTION AND REMEDIATION OF MICROBIAL SPOILAGE AND CORROSION IN AVIATION KEROSENE – FROM REFINERY TO WING
Edward C. Hill and Graham C. Hill

There is increasing evidence of an increase in the incidence of microbial fouling and spoilage of aviation kerosene and of fouling and corrosion of storage tanks, distribution systems and aircraft. The possible reasons for this are reviewed and the anti-microbial strategies currently available are described and critically examined. Some strategies are not well known and are therefore not yet widely deployed. Microbes can now be detected quantitatively on site and an early warning obtained of impending microbial problems. Appropriate anti-microbial actions can then be used to avert operational problems. A diversity of proprietary test kits is now available for the assessment of microbial contamination in fuel tanks and fuel systems and in associated water and these are described. Most give semi-quantitative or quantitative estimates of the number of viable (live) micro-organisms present although a few measure other parameters which can be related to the extent and/or significance of contamination. By careful consideration of the objectives of the microbiological test programme, the facilities and time available for testing and the advantages and limitations of the various test methods available, it is possible to make a selection of the most suitable test procedures and decide their frequency of use. Whatever the method or methods selected the results will only be as good as the quality of the sample. Sampling locations and sampling procedures will have considerable bearing on the results of testing and on the interpretation of results. Microbiological monitoring on site is the key to successful anti-microbial procedures at all stages of fuel distribution and use. Maintenance manuals for different aircraft frequently advocate (or mandate) different precautionary or corrective strategies. These will be discussed and current suggestions for harmonisation described.

USING TETRAKISHYDROXYMETHYL PHOSPHONIUM SULFATE (THPS) FOR THE CONTROL OF HYDROGEN SULFIDE IN CRUDE OIL STORAGE SYSTEMS

Howard L. Chesneau

Tetrakishydroxymethyl Phosphonium Sulfate (THPS) is becoming a widely used bactericide in oil field production for the control of H2S. The application has been so successful that its merits need to be explored as an alternative to conventional biocides currently being used in crude oil storage systems. Unlike a number of other bactericides, THPS is not inactivated by hydrogen sulfide and consequently can remain active under severe anaerobic conditions. THPS have been found to be effective in both acid and alkaline environments. THPS is unusually benign in the environment and degrades rapidly into non-toxic compounds. This paper will discuss the technical merits and findings using THPS in various aerobic situations in the field.

INVESTIGATION OF FACTORS AFFECTING THE SPOILAGE SUSCEPTIBILITY OF FUELS WITH A VIEW TO DEVELOPMENT OF A FUEL BIOVULNERABILITY TEST

Graham C. Hill1, Barry Herbert, Joachim W.J. Koenig and R.N. Smith

The Microbiology Committee of the Institute of Petroleum, London has established that there would be considerable merit in developing a test procedure which would enable the assessment of the inherent susceptibility of distillate fuels to microbial spoilage (biovulnerability). Such a method would be of particular use to long term strategic storers of fuels but would also benefit end users and those responsible for maintaining distribution facilities. It was proposed that a test based upon the quantification of water extractable carbon, nitrogen and / or phosphorus in fuel could give an assessment of biovulnerability. The importance of nitrogen and phosphorus in determining extent and rate of growth is well documented for many microbial environments.

This investigation hoped to establish the relative importance of nitrogen and phosphorus derived from the fuel itself (for example from additives) as opposed to nitrogen and phosphorus from environmental contamination in determining biovulnerability. A range of fuel samples were assayed for water extractable carbon, nitrogen and phosphorus by measuring these elements in water shaken with the fuel using a standard aqueous extraction procedure. This data was compared to the results of Biochemical Oxygen Demand tests of extractant water prepared using the same procedure. The fuels were also tested for their ability to support microbial growth when placed over water phases with and without nitrogen and phosphorus supplementation.

NEW GUIDES FOR DIAGNOSING AND CONTROLLING MICROBIAL CONTAMINATION IN FUELS AND FUEL SYSTEMS

Frederick J. Passman, Ph.D.

Recently, the Institute of Petroleum (IP), London and the ASTM have created standard guides addressing fuel and fuel system biodeterioration. Although the documents have much in common, they were written for different audiences, as reflected in the respective guides' style. This paper addresses the philosophy behind the ASTM document, D6469 Guide to Microbial Contamination in Fuels and Fuel Systems. It also summarizes D6469's contents. D6469 places microbial contamination in the context of more general root cause analysis. Consequently, it was written for three stakeholder groups involved in fuel and fuel system stewardship: managers, field service personnel and laboratory technicians. Following ASTM's style guidelines, D6469 provides an extensive list of references to relevant practices and test methods. It also includes a glossary of terms unfamiliar to non-microbiologists. An executive overview, summarizing the nature, detection and control of microbial contamination precedes more detailed, topic specific sections.

CONTROL OF DETERIOGENIC BIOFILMS IN DIESEL/WATER SYSTEMS

Angela G. Menendez and Christine C. Gaylarde

The effect of coating steel surfaces with an anti-corrosive epoxy paint with or without an isothiazolone biocide was studied with respect to biofilm formation in model diesel/water systems. The adhesion of sulfate-reducing bacteria (SRB) and various fungi, all isolated from contaminated diesel storage tanks, was measured using epifluorescence microscopy. SRB were the most adhesive organisms, producing uncountable cell numbers on the surfaces of all coupons after 3 days. SRB and the fungus Hormoconis resinae adhered preferentially to uncoated steel surfaces ($P<5\%$). Their numbers were reduced on painted surfaces and even further reduced when an isothiazolone biocide (Sea Nine) at 0.3 or 1.0% was included in the paint formulation. The filamentous fungi, Aspergillus fumigatus and Paecilomyces variotii, and the yeast, Rhodotorula glutinis, all showed higher sessile numbers on coated than on uncoated surfaces. Atomic force microscopy suggested that paint film was degraded in contaminated systems. P. variotii was the most susceptible fungus to the biocide, while R. glutinis numbers increased when 0.3% biocide was included in the paint. These results show that microbial biofilm formation in diesel fuel storage tanks may be increased by coating with anti-corrosive epoxy paints. Biofilm can be controlled, but not completely avoided, by including in the paint formulation the isothiazolone biocide used in this study.

SESSION 8: AVIATION FUELS - I: CONTAMINATION AND HANDLING

IMPACT OF RED-DYE CONTAMINATION ON THE THERMAL STABILITY OF JET FUEL

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

An experimental study of the effect on diesel-fuel red dye on the thermal stability of jet fuel has been undertaken by the FAA with multiple sponsorship including the DESC, the Airline Transport Association, and the engine and airframe manufacturers. The program has two objectives:

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

The effort to meet the first objective consists of two phases: 1) a screening effort to identify and select a test fuel that has a thermal stability that is sensitive to red dye, and 2) a series of fuel-nozzle fouling tests to quantify the effect of the red dye and diesel fuel in terms of reductions in the fouling life of engine hardware. This paper reviews the tests and analyses of the first phase in which 19 jet fuels of different crude source and processing history were evaluated for sensitivity to red dye. Two methods of quantifying JFTOT results were used: 1) the breakpoint temperature and 2) deposit thickness. The results are discussed along with the selection process for the test fuel to be used in the second phase of hardware testing.

A SURVEY OF SOLID CONTAMINANT TYPES AND LEVELS FOUND IN A RANGE OF AIRPORT FUEL HANDLING SYSTEMS

Vic B. Hughes and Phil D. Rugen

Particulate contamination (particles >0.8 µm) of jet fuels from a selection of airports world-wide has been assessed in terms of concentration levels (by a gravimetric membrane method) and composition (using X-ray diffraction and/or fluorescence techniques). Within each selected airport, samples were taken from the upstream side of filters in the receipt, out-of-storage and into-plane positions. The study was limited to single samples from each position at each airport and as such provides only a snapshot of the contamination situation. This study was funded by the American Petroleum Institute in a co-operative venture with the Institute of Petroleum.

AVIATION FUEL HANDLING: SPECIFICATIONS CONTROLLING THE PERFORMANCE OF FILTER UNITS USED IN A JET FUEL DISTRIBUTION SYSTEM

Phillip D. Rugen

The cleanliness of Jet fuel is ensured by the fuel passing through many different filtration units on its journey from refinery to aircraft. These units, capable of removing dirt and water, use several different types of filter ranging from a simple Sieve or Microfilter to a Filter Water

Separator or Water absorbent Monitor. The minimum performance requirements of such units are outlined in several recognised Industry specifications issued by the American Petroleum Institute (API) and the Institute of Petroleum (IP). The increasing demand for reliable filtration equipment to maintain fuel cleanliness, particularly in highly surfactant laden fuels, has led to improved specifications and the development of safer, more efficient filtration units. This paper will review the history of the specifications, outline some of the major changes and highlight some of the future challenges that the introduction of new additives will bring, in particular in the contaminant removal process.

LOW TEMPERATURE PROPERTIES FOR JET FUEL – PROBLEMS AND SOLUTIONS

Kurt H. Strauss, Consultant

The paper describes low temperature problems caused by fuel and by water. Fuel problems can involve the precipitation of waxy components from the fuel, thereby creating two phase flow and leaving an unpumpable, semisolid fuel-in-wax emulsion layer on the bottom of aircraft fuel tanks. At very low temperatures the increase in fuel viscosity above a certain limit can prevent ground starting or engine altitude relight. Current solutions to wax formation include the adjustment of flight routing as well as proposals to lower fuel freezing point and viscosity. A program of measuring fuel freezing point as the fuel is being loaded on aircraft is described. Research is underway to study and solve the problems resulting from allowing two phase flow in the aircraft. Keeping free water in fuel at minimum levels is a major part of ground quality control. Water-caused problems onboard aircraft are usually due to trace levels of water coming out of solution and freezing into ice which can plug filters or other tight clearances. Ice formation on board the aircraft is prevented by fuel additives, heating parts of the fuel system or relocating critical components into warmer locations. Water-caused problems at elevated temperatures, such as microbial growth, are not covered in the paper.

CLAY FILTRATION OF JET FUELS CONTAINING STADIS® 450 AND OTHER ADDITIVES OR IMPURITIES

Cyrus P. Henry Jr. and Neva Montgomery

In the USA, clay filtration is commonly used in distribution systems to remove surfactants and some other trace materials from jet fuels that may have been introduced during transport from refineries. This is particularly useful when fuel has been transported by common product pipeline, or other means where some level of trace contamination may have occurred. The primary purpose of such clay filtration is to remove surfactants that might affect the water-separating capability of the filter coalescers used at airport receipt and during fueling of aircraft.
Use of Stadis® 450 in jet fuels that may be clay filtered is a major concern, and barrier, to use of the additive in US jet fuels. Studies were undertaken to determine how quickly breakthrough of Stadis® 450 might occur, and the consequences for absorption of other impurities or additives when Stadis® 450 is present in jet fuels.

SESSION 9: AVIATION FUELS - II: JP8+100 and JFTOT STUDIES

ELECTRICAL CONDUCTIVITY OF JP8+100 ADDITIVES IN HYDROCARBONS AND FUEL

Brian Dacre, Janice I. Hetherington and Rogers Longjohn

The electrical conductivity requirement for military jet fuels is currently met by use of the static dissipator additive Stadis 450. Certain additives, whose prime purpose is to perform as “high temperature thermal stability additives” and which were submitted as candidates for the JP8+100 Programme, are also capable of increasing the electrical conductivity of hydrocarbons. The paper reports on a conductivity study that has concentrated on four HITTS additive packages chosen for their different chemistries. The work aims to provide a general view of their behaviour via measurements on the effects of a variety of factors. Conductivities have been measured in dodecane and a non-additised JP-8 fuel. These data and data on the effects of co-additives, other possible fuel components and temperature, over the range 0°C to +50°C, are discussed.

CONDUCTIVITY AND CHARGING TENDENCY OF JP-8 + 100 JET FUEL

Joseph T. Leonard and Dennis R. Hardy

The effect of the Betz Themal Stability Additive, 8Q492, and the Octel Static Dissipater Additive, Stadis 450, on the electrical conductivity and electrostatic charging tendency of Jet A fuels was examined. Fuel conductivity was measured using the Emcee Precision Conductivity Meter and charging tendency using the EXXON Mini-Static Tester. A variety of filter media were used to assess charging tendency including the Type 10 reference filter paper and filter media from fuel coalescers, separators, monitors and reticulated foam. Fuels were found to vary widely in their response to Stadis 450. At a concentration of 1ppm, Stadis 450 increased the conductivity of Jet A fuels, on average, 138 pS/m. If the fuel also contained the Betz additive, the average conductivity increase was 252 pS/m. It was found that the Betz additive, at a concentration of 256 mg/I, increased the conductivity of most fuels to above 100 pS/m and of 15% of the fuels above 150 pS/m which is the lower specification limit for JP-8 fuels. The Betz additive increased the charging tendency to very high levels on only two media, namely, the Type 10 reference filter and a coalescer medium. Charging on all other media including both the non-conductive and conductive reticulated foams was quite low. Fuels containing Stadis 450 exhibited high charging on most coalescer media, particularly fiberglass and felt, and on the media paper and superabsorbent and absorbent media of the monitor cartridge. They also gave high charging on both the conductive and non-conductive foams, but not on the separator media or on the Type 10 reference filter. It should be emphasized that all of the filter media tested were designed for use with the Betz additive and may or may not be representative of the media being used with fuels containing Stadis 450 today.

DEVELOPMENT OF A LOW TEMPERATURE JET FUEL

Cynthia A. Obringer, Jamie S. Ervin, Steven Zabarnick, and Kenneth E. Binns

The U.S. Air Force is developing an inexpensive low-temperature JP-8 fuel that can be used at temperatures as low as –53 °C. Currently, Jet A is used at temperatures above -40 °C, and the use of Jet A-1 and JP-8 is limited to temperatures above –47 oC. Costly specialty fuels, such as JPTS, are used when temperatures below 47 °C are likely to be encountered. The current effort has several facets: fundamental studies of jet fuel crystallization, low-temperature fuel system simulation and modeling, fuel system material compatibility, engine and flight tests, and additive field implementation.

STRATEGIES AND MATERIALS FOR THE REMOVAL OF SPEC•AID 8Q462 DISPERSANT FROM JP-8+100 AVIATION TURBINE FUELS

W. L. Parker and Nancy R. Calvert

The watershed qualities of jet fuel are negatively impacted by the dispersant component of SPEC•AID 8Q462 . The dispersant also degrades the effectiveness of existing water removal components of the fuel handling system. This has led to the practice of injecting the additive to the fuel at the wing and precludes return of JP-8 +100 fuel to the general fuel pool. We describe efforts to design a mechanism for removal of the dispersant part of the SPEC•AID 8Q462 package from JP-8+100 treated fuels. This talk will focus on the materials aspect of different removal strategies and include discussions of the potential impacts of removal strategies on the base fuel thermal stability.

USE OF THE JFTOT FOR THE EVALUATION OF POTENTIAL THERMAL STABILITY ADDITIVES

Samantha Marshall, John D. Scrivens and Spencer E. Taylor

The Jet Fuel Thermal Oxidation Tester (JFTOT) and related instruments have been used for many years to determine the thermal stability of liquid fuels. The principal application of the JFTOT is as a specification test method for jet fuel thermal stability. In the present work, however, we have used the JFTOT as a research tool in our continuing studies into the evaluation of jet fuel thermal stability additives. We have been particularly concerned with the ability of additives both to reduce the tendency for surface deposition on metal surfaces, as well as preventing the formation of insoluble particulates in the thermally-stressed bulk fuel. To this end, we have used the JFTOT for quantifying surface deposition (in conjunction with ellipsometric analysis of deposit thickness) with simultaneous analysis of the rate of differential pressure increase as a measure of bulk particulate formation. This “dual parameter” approach has enabled the performance of different potential thermal stability additives to be “mapped” in terms of their ability to control both surface and bulk deposition. This has provided a convenient and valuable means of quantifying thermal stabilization using additive formulations. Specifically, the results are considered in terms of factors influencing classical nucleation and growth processes taking place in the bulk fuel and on the JFTOT tube surface involving deposit precursors.

EXPERIMENTAL EVALUATION OF THE TWO-TIERED JFTOT TEMPERATURE PROVISION FOR JET A FUEL

Clifford A. Moses, Stan Seto, and Patti Liberio

Experimental results are reported from a series of deposition experiments conducted with actual aircraft engine fuel nozzles to determine the significance of a decrease in thermal stability of 15°C on the fouling rate/life of the test nozzles. The effects of the JP-8+100 additive package on The results is also addressed.

SESSION 10: AVIATION FUELS - III: ADDITIVE USE & OTHER STUDIES

THE DEVELOPMENT AND USE OF METAL DEACTIVATORS IN THE PETROLEUM INDUSTRY: A REVIEW

J. Andrew Waynick

The development of metal deactivator additives for the petroleum industry is reviewed from the first additive used in gasoline to the present. The chemistry of how these additives are thought to work is detailed and related to chemical structure. Discussions of the three mechanisms attributed to metal deactivators - chelation, surface passivation, and bulk phase reactivity - are provided. In this regard, special emphasis is given to the metal deactivator N,N'-di-salicylidene-1,2-propane diamine (MDA) in aviation turbine fuels. Previously reported work, especially work from 1991 to the present, investigating the impact of MDA on jet fuel thermal stability is reviewed.

STUDIES OF JET FUEL FREEZING AND COLD FLOW IMPROVING ADDITIVES BY DIFFERENTIAL SCANNING CALORIMETRY

Steven Zabarnick, Nikki Widmor, Jamie S. Ervin, and Cindy Obringer

We have used differential scanning calorimetry (DSC) to study the freezing of jet fuel and the effect of cold flow improving additives. We find that the cooling (freezing) exotherm is a more useful diagnostic tool for this purpose than the heating (melting) endotherm. Jet fuels (Jet A, JP 8, and Jet A-1) display a strong exotherm upon cooling between -45 and -60 °C. By the study of mixtures composed of classes of jet fuel components (normal paraffins, isoparaffins, and aromatics), we find that the cooling exotherm is primarily due to the liquid-solid phase change of the normal paraffins. Cold flow improving additives (e.g., pour point depressants) show only small effects on the DSC exotherm despite large effects observed in cold flow devices. This indicates that these additives work primarily by affecting the structure of the alkane crystals. This is supported by low temperature microscopy studies. We have also studied the use of treating jet fuel with urea to selectively remove large normal alkanes. DSC studies show large decreases in the temperature of the cooling exotherm upon urea treatment.

STORAGE AND OXIDATIVE STABILITY OF JET FUEL RT BLENDED WITH HITEC-580

Zhetcho D. Kalitchin, Margarita I. Boneva, Snezhana A. Uzunova, Evgeni S. Mladenov, Georgi K. Botev

The influence of HITEC-580 additive on the formation of existent gums and the acidity of jet fuel RT at storage, has been investigated under real conditions. The results show that the taken by us value, for limit concentration of HITEC - 580 to 15 mg/l is reached after the 80-th day of storage. Obviously, in this period of time the jet fuel may be used without loosing its antiwear properties to a great extend. The changes of the existent gum and acidity are within the requirements of the standard. The influence of the additive on some oxidation parameters of a sample of unblended jet fuel under thermal stress has been evaluated. A synergistic effect has been observed between HITEC-580 and 3-methyl-1-phenyl-4-palmitoyl-pyrazolone-5, regarding the hydroperoxide decomposition to free radicals.

EVALUATION OF THERMAL STABILITY IMPROVING ADDITIVES FOR JET FUEL IN BOTH LAMINAR AND TURBULENT FLOW TEST UNITS

John E. Colbert and Clarence J. Nowack

The Naval Air Systems Command has evaluated the individual benefits of three (3) different thermal stability improving additives (TSIAs) in jet fuel using two (2) separate, small-scale test devices - one laminar flow and the other turbulent. Both systems pump fuel at constant flowrate and use stainless steel tubes that are heated to maintain the bulk fuel at a constant, elevated test temperature. The laminar device has an inside diameter of 0.1 inches (0.262 cm) and an approximate Reynolds Number of 200, whereas the turbulent has an inside diameter of 0.01 inches (0.0254 cm) and a Reynolds Number of 13,000. The results have shown that all three (3) TSIAs, when tested at their maximum dose levels, reduce the amount of thermal deposits (measured via carbon burnoff) in both flow regimes for three (3) different base fuels tested. Both units rank the level of thermal stability in the same order for the 3 baseline fuels tested. In addition, both devices show that Betz 8Q462 is the most effective additive of the three tested, with MDA demonstrating almost similar performance in controlling deposit formation. Furthermore, Betz 8Q406 was not as effective as the two other additives, but a change in its formulation by the addition of 2 mg/l MDA (to produce 8Q462) greatly improved its performance in both test devices, but most notably in the laminar unit. However, one exception had occurred when MDA was added to one of the test fuels (Tank 20/22), which caused an increase in deposition compared to the neat fuel when tested in the turbulent unit. Overall, the combination of the accelerated test conditions in the turbulent unit of higher bulk fuel temperature, higher flowrate, turbulent flow (i.e., flatter temperature profile across the tube ID), and shorter residence time make this a more severe test when compared to the laminar device.

LUBRICITY SURVEY OF HYDROTREATED AND HYDROCRACKED JET FUEL COMPONENTS

Alexandra Ebbinghaus, Joanna M. Bauldreay, and Taous Grandvallet

The latest edition of the Jet A-1 specification DEF-STAN 91-91/Issue 3 includes a lubricity specification which comes into effect on 1st December 2000 and applies at the point of manufacture. Lubricity is measured using the Ball-on-Cylinder Lubricity Evaluator (ASTM D5001) and a maximum wear scar diameter limit of 0.85 mm is set. The requirement to determine lubricity applies only to fuels containing more than 95% hydroprocessed material where at least 20% of this is severely hydroprocessed (i.e. subjected to a hydrogen partial pressure greater than 70 bar) and for all fuels containing synthetic components. Results of two surveys, the first concentrating on a selection of jet fuels and the second on refinery jet fuel blending streams, e.g. straight run, hydrotreated and hydrocracked kerosene components, are discussed in view of this requirement. As expected hydrocracked samples have very poor lubricity with wear scar diameters between 0.90 and 1.12 mm. Unexpectedly, a number of the hydrotreated samples also had poor lubricity with wear scar diameter up to 0.99 mm. Non-linear improvement of lubricity was observed when high lubricity straight run material was blended with the hydrotreated and hydrocracked material.

CONTINUING STUDIES OF SINGLE FIBRE WETTABILITY TO MODEL SURFACTANT INTERACTIONS IN COALESCERS

Spencer E. Taylor

The removal of water from jet fuels is a key requirement for the continued safe and successful operation of aircraft engine and fuel management systems. We have been interested in the interactions occurring at the microscopic level at the different interfaces existing within the complex fuel/water/coalescer system. A previous IASH paper described a novel single-fibre approach in which coalescer fibre wettability was considered experimentally in the three-phase contact region, as would be the case in practice. This earlier work used untreated glass fibres in the presence and absence of surfactants; the present work extends this approach to single fibres modified to contain solidified “droplets” of hydrophobic resin, as found in most commercial coalescers. This has provided an insight into the wetting behaviour of individual fibres in the presence and absence of FSII [di(ethylene glycol) monomethylether], to provide a microscopic analogy with the practical situation. The findings are discussed in terms of possible effects on the coalescence process and consequent coalescer performance.

SESSION 11: GAS TURBINE AND AVIATION FUELS: GENERAL PAPERS

CROSSFLOW FILTRATION DEVELOPMENT FOR FUEL CLEAN UP SYSTEMS IN WARSHIPS.

Barry C H Drew and Stephen R Churchill

DERA, Fluid Systems Engineering, Haslar, Gosport, Hants, PO12 2AG, England

Gas Turbine (GT) propulsion currently predominates in the surface warship Fleet. A multistaged fuel clean up system helps protect the GT from contaminants in the fuel. However, the fuel clean up system is costly to build run and maintain. Replacing it with a simple and environmentally friendly crossflow system gives substantial savings in through life costs. Initial short term scoping tests on single ceramic crossflow filter elements with “dry” and test fuels wet with seawater established the preferred pore sizes and threshold pressures at laminar and turbulent flows. Additionally, the effects that temperature and slugs of seawater in the fuel have on performance were investigated. Slugs of seawater in the fuel briefly reduced permeate quality otherwise clean fuel was produced. Providing the permeate flow was sustainable economic systems could be designed to meet warships requirements. Confidence in sustaining fuel quality and flow was demonstrated through long term single element tests. These tests indicated that a warship could be deployed for up to one year whilst still meeting full power requirements. A simple, fit and forget crossflow system design is preferred. Crossflow filtration allows different options ranging from, a basic system with a large number of elements, to a less basic system using a minimum number of elements. The less basic system would run with a higher transmembrane pressure (TMP) and require the means for reducing the rate of fouling as well as cleaning fouled elements. Warships operate in cold or hot climates and in emergencies accept low quality fuel. These parameters are considered in choosing the number of filter elements and the level of systems required for a space saving and economic design. The performance of a land based part scaled up system has been used to investigate options best suited to warship operations before conducting sea trials on a prototype now being built. Application to GT powered vessels such as ferries and cruise liners are also envisaged.

FACTORS INFLUENCING THE RESULTS OBTAINED BY THE HIGH REYNOLDS NUMBER THERMAL STABILITY TEST INSTRUMENT (HiReTS)

Mike Sherratt, John Wood, Joanna Bauldreay and Richard HeinS

The HiReTS instrument is being developed as an alternative to the traditional JFTOT test for measuring the thermal stability of gas turbine fuels. This instrument offers results in numerical form while realistically testing the fluid in the turbulent flow regime. The inclusion of such a procedure into specifications will require the agreement of a numerical value to determine whether a test sample passes or is rejected. The results of a test will be affected by a number of factors such as sample type and preparation, test temperature, flow rates, pressure and capillary tube characteristics. These contributory factors influence the correlation of the HiReTS results with other procedures, and the performance demonstrated in inter-laboratory test programmes.

FLOW VISUALIZATION OF THE FREEZING OF JET FUEL
D.L. Atkins, J.S. Ervin, M. Vangsness, and Cindy Obringer

The objective of this research is to obtain images of the freezing of hydrocarbon fuels within a simple flow to assist understanding of the interaction between the flow and phase-change dynamics. JPTS, kerosene, Jet A, additized kerosene, and additized Jet A samples were cooled in a rectangular, aluminum chamber with quartz viewing windows. Images and surface temperatures were recorded during the solidification process. The images tracked the advancing freezing front and the influence of the buoyancy-driven flow. Cooling of JPTS resulted in the lowest volume of wax formation on the chamber surfaces. In contrast, the freezing of kerosene yielded the greatest volume of wax formation. Jet A and kerosene samples containing a low-temperature additive exhibited a smaller volume of deposited solids than did the neat fuel samples. However, the additized fuels developed a significant population of suspended particles.

QUEST FOR A RELIABLE METHOD FOR DETERMINING AVIATION FUEL THERMAL STABILITY: COMPARISON OF TURBULENT AND LAMINAR FLOW TEST DEVICES
Seetar G. Pande, Richard A. Kamin, Dennis R. Hardy, Clarence J. Nowack, John E. Colbert, Robert E. Morris, and Lucio Salvucci

Thermal deposition, based on carbon burn off, was evaluated in two turbulent flow and one laminar flow test devices. The two turbulent flow test devices were the Navy Aviation Fuel Thermal Stability Simulator (NAFTSS), developed by Rolls Royce, UK, for the US Navy, and the High Reynolds Number Thermal Stability (HiReTS) bench rig - developed by Shell Research and Technology Centre, UK. The laminar flow test device was the Tubular Reactor (TR) - a bench rig developed by the Naval Air Systems Command Air-4.4.5 (NAVAIR). Three jet fuels were used in the comparison of the NAFTSS and the TR, and six fuels (five jet and one diesel) in the comparison of the HiReTS and the TR. The data employed were generated by NAVAIR. Good correlations were obtained among the two turbulent flow and the laminar flow test devices. A possible explanation of these results is that for the fuels examined, Reynolds number does not appear to be a critical factor in predicting thermal stability. These results are significant for they validate the use of laminar flow in devices such as the specification test method, i.e., the JFTOT, ASTM D3241. Furthermore, based on our evaluation of the test devices examined, we postulate that fuel temperature is likely the critical factor in predicting jet fuel thermal stability, as long as attention is paid to residence time and thermal gradients of the hot section.

DEPOSITION OF AVIATION FUEL TRICYCLIC AROMATIC COMPOUNDS ON HOT METAL SURFACES IN AN AIRCRAFT FUEL SYSTEM
Paul M Rawson, Alan J Power and Michael G O'Connell

A chemical mechanism has been observed that may contribute to jet fuel thermal deposits on hot metal surfaces. It has been found that refinery hydrogenation of aviation fuels containing trace quantities of isomers of methylanthracenes and methylphenanthrenes, compounds that are known to be present as trace components in jet fuel, are converted into 1,2,3,4,5,6,7,8-octahydro derivatives of the parent tricyclic aromatics. These hydrogenated fuel components are soluble in aviation fuel, whereas the methylanthracenes and methylphenanthrenes have relatively low solubility. Only the central fused ring remains unhydrogenated, and in what are believed to be oxidative, endothermic reactions, these hydrogenated fuel components were found to deposit as methylanthracenes / methylphenanthrenes on hot fuel / oil heat exchanger surfaces in a military aircraft. Thus, while hydrogenation of jet fuel significantly improves overall thermal stability of the fuel type, as measured using laboratory test rigs, this process may produce fuel components that, over time, form detrimental deposits on hot metal surfaces in fuel systems of gas turbine powered aircraft. Preliminary, limited, aromatisation laboratory studies to investigate a conversion rate of the specific hydroaromatic compounds into their dehydrogenated aromatic analogues were conducted using multiple passes of a hydrotreated light cycle oil fraction at elevated tube fuel/wall temperatures. Molecular conversion rates of octahydromethylanthracene to methylanthracene were observed to occur, with percentage ratios of methylanthracene to octahydromethylanthracene changing in a positive direction for methylanthracene formation of between about 8-23%, after limited passes through a heated circulating jet fuel system. Evidence gained to date indicates that these trace PAHs in jet fuel are deposited on the heat exchanger surfaces over many hundreds of hours of heat exchanger service, and thus, after passage of many millions of litres of fuel containing the precursors.

SESSION 12: POSTER SESSION

PHOTOEFFECTS DURING PRODUCTION, TRANSPORTATION, STORAGE, ANALYSIS, AND EXPLOITATION OF LIQUID FUELS

S.K.Ivanov

Photoeffects in liquid fuels arise during their production, transportation, storage, analysis and exploitation in the internal-combustion engines. The photoeffects are indebted to the following interactions of the fuels:

- an interaction between fuels and metal surfaces and appearance of triboluminescence and tribochemiluminescence
- an interaction between fuels and mechanical deposits or fine water particles and air during staying and storage, resulting in electrical discharges and flashes
- the oxidation of fuels during their storage and transportation and an accumulation of peroxides and peroxy radicals, causing chemiluminescence
- external photoeffects on the fuels during their analysis
- photoeffects in interanl-combustion engines: electric discharges and photoemissions resulting from combustion processes.

The photoeffects may affect directly the metal surfaces, or/and additives and hydrocarbons on the surface and in the volume of the combustion system. The assessment of photoeffects in interanl-combustion engines is made in relation to the appearance of additional pollutants of air, soils and water.

GASOLINE BLENDSTOCK STABILITY

F.Panarello, G.Boni and S. Guanziroli

The instability of particular gasoline blendstocks as cracked naphtha is well known and generally related to olefin content and storage condition. The most important parameters in evaluating stability on storage of gasoline are existent gum (ASTM D381) and oxidation stability (ASTM D525 and 873). Straight run and hydrocracked gasoline blendstocks are generally used as reforming feedstocks. A problem of fouling in a reforming heat exchanger came up in a plant in Italy when processing in hydrogen atmosphere a particular stream supplied to the refinery by ship with a potential problem of pollution. Accurate analysis of critical stream was performed according to the gasoline standard methods but no difference appeared with respect to non-critical gasoline feedstock. The above mentioned methods were then conveniently modified using accelerated conditions. Good indication was obtained on instability phenomena in processing condition, in particular in thermal conditions, allowing us to discriminate between different streams. Appropriate sampling of the critical feedstock was performed avoiding air contamination. The oxygen dissolved in gasoline at different tank level was quantified. A deep analysis of the heat exchange surface deposit was also performed including pyrolysis analysis. Four potential solutions of the fouling problem were identified: re-run in the topping unit of the refinery of the critical stream; blending with appropriate anti-oxidant additive; critical stream pre-hydrogenation in mild conditions; gasoline feedstock pre-treatment on adsorption media in order to prevent peroxides formation.

COMPARISON OF THE CHARACTERISTICS OF OIL SANDS DERIVED DIESEL FUELS AND THEIR BLENDS WITH CONVENTIONAL DIESEL FUELS

Craig Fairbridge, Yevgenia Briker, Zbigniew Ring, Parviz M. Rahimi, Ripudaman Malhotra, Michael J. Coggiola, and Steve E. Young

Detailed knowledge of the molecular composition of transportation fuels correlated with fuel combustion properties provides insight into improving the processing of different feeds and into designing future fuels. Diesel fuels produced from oil sands synthetic crude and from conventional crude oil were analyzed by gas chromatography-field ionization mass spectrometry and by liquid chromatography-gas chromatography/mass spectrometry. Analyses were presented in terms of hydrocarbon type for the total liquid fuel and in terms of hydrocarbon type distributed by the boiling point of the fuel. Diesel fuel derived from synthetic crude oil contained less total iso- plus normal paraffins and more total cycloparaffins than fuel derived from conventional crude oil. Diesel fuel derived from synthetic crude oil also contained relatively more hydrocarbons in the higher boiling range. Gas chromatography-field ionization mass spectrometry presented additional information in terms of isoparaffin and normal paraffin contents.

C-STORES – THE REAL WORLD
Howard L. Chesneau

With changes in both gasoline reformulation and distribution in the United States, problems have begun occurring at the retail level known as C-Stores (Convenience Stores). These problems range from increasing amounts of particulates to severe corrosion. For the first time, the U.S. petroleum industry is currently entertaining final filtration specifications at the point of purchase. Increasing amounts of water has allowed unseen problems with biologicals and chemical interactions that have caused increasing concerns about the quality of delivered fuel. This poster will show visually some of these problems as discovered during tank cleaning operations.

LABORATORY THERMAL STABILITY TEST METHODS FOR AVIATION TURBINE FUEL: STATIC AND LAMINAR FLOW EVALUATIONS FOR JP8+100 THERMAL STABILITY

David R. Forester, George A. Malchow, Bharat B. Malik, George R.Wilson

With the progression of more demanding aviation turbine engines, coupled with the increasing demand for use of the fuel as a higher temperature heat sink, better definition of the thermal stability of jet fuels is expected. There are many tests that are designed to measure or assess thermal stability. The main concern for a given test is displaying sufficient discrimination to differentiate between fuels of average stability (JP-8) and intermediate stability (JP-8+100, JP-TS). This poster will describe the use of the ICOT and HLPS-DP as “concept thermal stability prediction” tools with aviation fuels, including Jet-A and JP-8, at JP8+100 test conditions. Also, the evaluation of thermal stability additives to improve thermal stability of these fuels will be presented. HLPS-DP tube deposit measurement using carbon burn-off (CBO) will be evaluated. Further, the initial evaluation of the HLPS-DP at extended test conditions, as a predictor for additive performance in extended tests, such as the EDTST, will be discussed.

STORAGE AND THERMAL STABILITY OF ULTRA LOW SULPHUR DIESEL FUELS
Ulla A. Kiiski, <u>Sari E. Laanti,</u> Seppo A. Mikkonen, and Pirjo A. Saikkonen

The answer as to whether or not increasing severity of hydrogenation improves or worsens storage stability has been unclear. The long-term storage stability of ultra-low (< 50 ppm) sulphur diesel fuels and fuel components were evaluated in this study. Also, the effect of blending differently processed components was investigated. The samples analyzed were produced under varying degrees of refining severity including straight run distillates, cracked components, moderately hydrotreated and severely hydrotreated components. Several methods were used to evaluate the long-term storage stability and some stability predicting methods were investigated such as extracting sediment precursors, SMORS (Soluble Macromolecular Oxidatively Reactive Species) in methanol. The results were compared to the current long term stability test methods; ASTM D2274 and a modified DuPont F-8-method, where samples are stored for 0...13 weeks at +50°C. All the products and most of the components were found to be very stable in laboratory tests. No effect whatsoever related to the severity of hydrotreating on stability was detected by any of methods used. The thermal stability of a fuel is an important property in modern diesel vehicles since fuel is exposed in the fuel injection system to higher temperatures (over +130°C) and higher pressures (over 1500 bar) than before. The fuel in the tank will also be heated up due to the fuel return line. This raised the question whether or not thermal stability is currently good enough and if 2-ethyl hexyl nitrate a common cetane improver, which is known to be thermally unstable, might decompose in the fuel system before entering combustion chamber. A high-performance diesel car of model year 1998 with a direct injection engine using a “common rail” fuel injection system was selected for the tests. Reformulated fuel was treated with an enhanced concentration of 2000 mg/kg of cetane improver. The car was driven 350 km in a dynamometer at +40°C ambient temperature at a speed of 130 km/h so that by the end of the test, the fuel tank was almost empty. The highest fuel temperature in fuel tank was +84°C and in fuel lines +98°C. Fuel from the tank was analyzed after the test for: cetane number, concentration of cetane improver, lubricity, viscosity, density, distillation curve, anticorrosion property, stability, color, cloud point and CFPP. The properties of the fuel sample were found to be practically the same as that of a fresh fuel. Thus, no deterioration of fuel or decomposition of cetane improver or other additives was found (J. Ahola, Fuel Requirements of High-Pressure Fuel Injection Equipment of Diesel Passenger Cars. Master’s Thesis. Helsinki University of Technology, 1999. 64 p. in Finnish). Reformulated diesel fuel “Citydiesel” (sulphur < 50 mg/kg, total aromatics < 20 vol-%) has been used commercially in Finland since 1993. Experience has shown that the severely hydrotreated diesel fuels have been very stable and have operated without any stability related or other problems.

FOCUS ON ALTERNATIVE FUELS GAS TO LIQUIDS AS POTENTIAL MILITARY FUELS

Leo L. Stavinoha

Automotive and aircraft fuel is usually a commodity that is assumed to be a given in discussions of operability of fielded ground vehicles. Fuels from current natural gas-to-liquids (GTL) conversion processes (Fischer-Tropsch liquid fuels (FTL)) offer the possibility to be produced from processors mounted on barges and operated in remote locations. This potentially attractive methodology for making synthetic liquid fuels could be used by the military or relief forces in distressed areas. Logistically, it is preferable to obtain liquid fuels in the location where they are to be consumed. FTL generally is free of sulfur and aromatics and is composed of paraffins (contributing to a high cetane number), which provides an attractive "clean" fuel for compression ignition diesel engines. These favorable properties assist as a fuel enabler to future low emission vehicles with compression ignition (CI) engines employing exhaust gas recirculation (EGR) and pollution reduction treatment devices. For similar reasons, it may be an attractive fuel for use in sulfur sensitive fuel cell reformers. However, simple hydrotreated FTL processes may require additional refining to reduce wax-forming normal paraffin content in order to meet Army ground/aircraft fuel cold flow properties. Military diesel and jet fuels are procured under Commercial Item Description (CID) A A 52557 (based on ASTM D 975) and MIL DTL 83133/MIL-DTL-5624 (JP-8/JP-5), respectively. The Single Fuel Forward (single fuel in the battlefield) policy requires the use of JP-8 or JP-5 (JP 8/5), which has the same low temperature freeze point requirement as commercial aircraft Jet A-1 (ASTM D1655).

This report is particularly useful to future combat systems and truck designers as it places in perspective considerations related to fuel property effects on diesel engine performance/durability, new engine/exhaust emission control technology, and military fuel requirements & policies. CI fuel properties (sulfur, cetane number, distillation properties, aromatics, elastomer compatibility, heat of combustion, cloud point/freeze point, density, lubricity/viscosity) are discussed in relation to FTL published information. Fuel properties crucial to fuel system/engine performance/operation are identified for both old and new combat/tactical and non-tactical vehicles. A summary of U.S. DOD position statements related to U.S. EPA proposed rules for 15 ppm sulfur limits for diesel fuel in 2007 are included.

BIODIESEL STABILITY TEST METHODS

Leo L. Stavinoha and Steve Howell

Modifications of ASTM 2274 Oxidation Stability of Distillate Fuel Oil (Accelerated Method), the ASTM D 6468 High Temperature Stability of Distillate Fuels (150°C) and ASTM D 4625 Distillate Fuel Storage Stability at 43°C were identified that may enhance their ability as useful tools to accurately and reliably predict the stability of biodiesel and biodiesel blends. Highly unsaturated biodiesel was found to be capable of dissolving cellulose ester porous filters used in ASTM D 2274. Use of 47mm diameter Whatman GF/F glass fiber filter (having a particle retention size of 0.7 micrometer) was found to be acceptable for use with all three of the methods. The thermal stability method was modified such that it could be used as a gravimetric test as opposed to a qualitative reflectance test since the biodiesel may not form light absorbing particulates for which the ASTM method was developed. Since biodiesel and biodiesel blends form acids and increase in viscosity as well as form filterable insolubles upon aging, both the ASTM D 2274 and D 4625 methods were modified to include measurement of total acids and viscosity increase of the fuel filtrate after aging. ASTM D 5304 for assessing Distillate Fuel Storage Stability by Oxygen Overpressure does not appear suitable for biodiesel or biodiesel blends as some readily absorb oxygen while not necessarily producing high sediment values invalidating the test method due to excessive pressure drop during the test due to oxygen absorption. Very stable biodiesel did not demonstrate rapid oxygen absorption. Oxygen absorption characteristics alone are not sufficient to predict magnitude of insolubles, acid number increase, or viscosity increase. However, in the cases where oxygen is not absorbed, minimal oxidation and oxidation related changes would occur. This property could be developed into a potential screening tool for applications where extended storage times are desired.

TRENDS IN THE PROPERTIES OF NATO MARINE DIESEL FUEL (F-76)

Stephen W. Wall, Andrew J. P. Ryan and Veronica Cloke Browne

Royal Navy gas turbine powered ships require a high-quality diesel fuel that exhibits good cleanliness and stability. The fuel that is purchased specifically for this purpose is designated by the NATO code F-76. For nearly two decades the Fuels and Lubricants Centre, Defence Evaluation and Research Agency has monitored the quality of all F-76 supplied to the British Royal Navy from European refineries and has observed significant changes in the properties of the fuel. This poster reviews these fuel property tends and relates these to changes in refinery processes.