1st INTERNATIONAL CONFERENCE ON LONG-TERM STORAGE STABILITIES OF LIQUID FUELS
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Abstract Summaries

SESSION 1: INTRODUCTION

OVERVIEW ON ASSESSMENT OF CRUDE OIL AND REFINED PRODUCT QUALITY DURING LONG-TERM STORAGE

Harry N. Giles, John N. Bowden and Leo L. Stavinoha

The underground storage of petroleum has been practiced for nearly seventy years, but only in recent years have large volumes of petroleum been stored for protracted periods. Considerable study has been devoted to the storage stability of finished distillate fuels such as gasoline and aviation turbine fuel but, until recently, little attention had been given to heavy fuels or to crude oil itself. The long-term strategic storage of crude oil was apparently first practiced by the Republic of South Africa; followed by the Federal Republic of Germany, France, Japan, and the United States. While most of these strategic reserves are in underground caverns, the Japanese are using surplus tankers for at least part of their storage, and the South Africans are using a combination of aboveground and underground storage. The strategic storage of refined products is practiced most notably in the Scandinavian countries of Norway, Finland, and Sweden. Other countries, such as France, Switzerland, the United Kingdom and the Federal Republic of Germany, are known to have finished product reserves bu.t, aside from West Germany, little is known of the quality of the products, in storage. This paper discusses tne results of studies, a number of which were sponsored by the U. S. Department of Energy's Strategic Petroleum Reserve Office, on the qualitative effects on petroleum resulting from prolonged storage primarily in deep underground caverns, bu.t also in aboveground tanks. These studies comprised a literature survey (Brinkman and others, 1980), discussions with scientific ·and technical personnel in various petroleum companies, and a comprehensive laboratory· investigation of samples from several strategic reserve sites in West Germany (Giles and Niederhoff, 1981). The references cited herein are not comprehensive or exhaustive, but give sources of more thorough discussion of. the topics covered. The personal communications cited generally refer to studies in progress.

UNDERGROUND STORAGE OF LARGE VOLUMES OF CRUDE OIL: THE U.S. STRATEGIC PETROLEUM RESERVE PROGRAM

Elliott L. Katz, Lawrence W. Vogel, Richard E. Smith

The impact of the oil embargo of 1973-74 demonstrated the need for a national strategic storage program to reduce the vulnerability of the United States to interruptions in oil imports. Accordingly, the Congress authorized the creation of a Strategic Petroleum Reserve (SPR) through enactment of the Energy Policy and Conservation Act (EPCA) (Reference 1) on December 22, 1975. The SPR was intended to demonstrate the will of the United States to insulate itself from the effects of disruptions of foreign oil supply, to avoid undue pressures on domestic and foreign policy caused by disruption of oil supply, to reduce the economic impact of the disruptions, and to allow the United States to fulfill its obligations under the International Energy Program. Other countries, notably Germany, France, and Japan, have also created national reserves to store petroleum products as well as crude oil as a hedge against short-term interruptions. EPCA provided for the storage of up to one billion barrels of crude oil in underground caverns[1] the locations of which would permit rapid distribution to critical refining centers by pipelines and tankers. The SPR funding, however, provides for the construction of storage facilities for 750 million barrels. No plans exist for developing storage for the final 250-million barrel increment. The approximate amount of oil in storage as of June 30, 1983, is 330 million barrels; at the present fill rate, the SPR will contain approximately 370 million barrels at the end of 1983, or about 100 days of supply in the event of a complete embargo of imported oil to the United States.

SESSION 2: THEORETICAL ASPECTS AND STATUS OF RESEARCH

ARMY DIESEL FUEL STABILITY AND CLEANLINESS

Maurice E. LePera, Leo L. Stavinoha, S.R. Westbrook and Sidney J. Lestz

Both background and current status of Army fuel stability and cleanliness-related programs currently underway at United States Army Mobility Equipment Research and Development Command (USAMERADCOM) and at U. S. Army Fuels and Lubricants Research Laboratory (AFLRL) are provided. These programs include: (1) the effects of environment/container on fuel quality; (2) development of laboratory and field performance test techniques; (3) fielding of diesel fuel stabilizer additives; (4) initiation of a worldwide Army diesel fuel quality assessment program; (5) identification of diesel fuel system debris, and (6) fuel-related field problem surveillance. As a part of this overview, identification of technical requirements/barriers has also been included.

H2S DIFFUSION IN AVTURS AND ITS INFLUENCE ON STORED FUELS

A.B. Shavit and J. Ben-Asher

Sulphiding of slipper pads of military aircrafts was widely reported in literature. Probably, the first cases were those of Canberra aircrafts operating in Malaya during 1956. Silver was completely removed from bearing surfaces within a few hours and consequently, serious pump failures were caused in operating those aircrafts. The corrosion was due to hydrogen sulphide (H_2S) liberated by sulphate reducing bacteria (SRB) in stagnant water bottoms of storage tanks. The corrosivity of fuels is measured by Standard Tests. The Copper Corrosion Test IP 154 or ASTM D-130 evaluates corrosivity by the discolourization of a polished copper strip, whereas the much more sensitive Silver Corrosion Test IP 227 by blackening of silver strip surface. The Silver Corrosion Test became mandatory in the British Jet Fuel Specifications "AVTUR" (Aviation Turbine Kerosene) D. ENG. R. D. 2494 (6) and in various other specifications.

Generally, the permissible limit for Copper Corrosion Test is lb, whereas the Silver Corrosion Test allows maximum 1. The object of this investigation was to study the influence of H2S diffusion from an aqueous phase, in an experimental diffusion column, on stored neat and phenolic type anti-oxidant inhibited AVTURS and its corrosive effect.

INSOLUBLE GUM FORMATION IN MIDDLE DISTILLATE FUELS

G. H. Lee and Leo L. Stavinoha

As a part of a basic research program to define the mechanisms of middle distillate fuel stability and additive inhibition, deleterious product formation using petroleum and shale-derived JP-5, shale-derived DFM, and Cat 1-H (1-G) engine reference fuel has been studied. Results to date are presented in this report. Insoluble materials in the form of particulate matter and adherent gums were studied with respect to both rate of formation and chemical composition. Aged and unaged fuels were also studied for changes in chemical composition. Particulate formation was studied in six size ranges from 0.5 um apparent diameter to >20 um. Overall particulate formation was determined by ASTM D2276. Adherent gums were measured gravimetrically. Chemical analysis was accomplished by HPLC, IR, GC/MS, UV, and elemental analysis for C, H, N, and S determined on selected samples. Comparison with data taken at other temperatures allowed the energy of activation (Ea) to be determined. As part of this program, a review of the current state-of-the-art in the field of middle distillate fuel stability studies was written and is appended to this report.

PROBLEMS ENCOUNTERED WITH BOTH LONG-TERM STORAGE AND HIGH TURNOVER MIDDLE DISTILLATE FUEL OIL

Howard L. Chesneau

In recent years the storage of middle distillate fuels, has become increasingly important. Problems such as microbial activity, fuel stability, and trace metals are becoming readily apparent at the end user level. Most current literature and guide lines suggest that water removal will eliminate additional need for microbial control, and that the rapid turnover of fuel negates problems caused by microbial activity and unstable fuels. The following cases are real world experiences documented over several years. The first concerns a large southern utility storing significant quantities of distillate fuel for gas turbine use. The second involves a fuel supplier to the commercial trucking industry and end user experiences.

HYDROPEROXIDE FORMATION IN JET FUELS

Robert N. Hazlett, James M. Hall, G.J. Nowack and Lynda Craig

Hydroperoxides in jet fuels have been recognized as the cause of degradation of aircraft fuel system elastomers. Laboratory studies indicated that a fuel with a peroxide number (P.N.) greater than one can be detrimental. Examination of fuels refined by different processes demonstrated that significantly higher peroxide numbers were obtained with fuels which had been severely hydrotreated. This phenomenon has been observed for jet fuels produced from petroleum and shale oil crudes. Hindered phenols at a concentration of 24 parts per million provided various degrees of protection against peroxidation. The best inhibition was found for phenols with t-butyl groups in both positions ortho to the phenol group. Peroxidation has been studied at several temperatures in the 43 to l00°C range. A variety of responses has been observed. In fact, each fuel exhibited a different pattern of peroxide number vs time. A JP-4 fuel without hydrotreatment rose rapidly to a low plateau. The other fuels rose to high levels followed by a sharp 9rop, a flattening out or a continued rise. A severely hydrotreated jet fuel without added antioxidant exhibited linear buildup of hydroperoxide with time at all temperatures. The same fuel and shale-derived jet fuel with antioxidant present, developed hydroperoxide in exponential fashion. Fuel behavior included induction periods, decrease of P.N. after attaining a maximum and stable peroxide level over long time periods. The extent of acceleration at a high temperature was not consistent, varying considerably with the fuel sample and the length of stress time. Cooperative test programs conducted by the Coordinating Research Council at l00°C found that individual laboratories obtained good repeatability for ROOH concentrations but reproducibility between laboratories was poor.

THE EFFECT OF ACCELERATED DEGRADATION OF GASOLINES ON CARBURETOR AND INTAKE VALVE DEPOSIT FORMATION

Edward Dimitroff and S. DeViney

The effect of long-term storage stability of hydrocarbon fuels, gasoline in particular, has received considerable attention for many years. Thus, a number of studies have been made on the mechanism of autoxidation of hydrocarbons in the liquid and vapor phases, and the literature contains much information on methods for the accelerated degradation of hydrocarbon fuels based on elevated temperature, use of catalysts, the action of oxygen, radiation, and others. However, gasoline stability investigations have been conducted with a limited number of fuels, and the test methods used were mostly concerned with the prediction of storage stability in terms of gum formation. Less attention has been devoted to the effect that this gum has on engine performance, in particular to carburetor and intake valve deposition. Thus, the relationship of high gum content to engine deposition has been implied by means of laboratory bench investigations and limited field tests, but no full-size engine performance evaluations of any significance have been conducted with fuels that have undergone accelerated degradation. Probably, such information is not available because, to be meaningful, it requires that a great number of fuels, available throughout the U.S.A., be subjected to largescale degradation so that sufficient quantity of degraded fuel is obtained for engine testing. Moreover, not until recently, laboratory engine tests were made available to carry out such investigations.

SESSION 3: LONG TERM STORAGE STABILITIES OF FUELS DERIVED FROM OIL SHALES AND COAL

STABILITIES OF FUELS DERIVED FROM COAL, OIL SHALE AND PETROLEUM

Norman C. Li, Robert N. Hazlett, L. Jones, G. Ge, N. F. Jaggi and C. M. White

Storage stabilities of upgraded coal-derived liquids (H-coal, SRC-II) and JP-5 jet fuels derived from petroleum and oil shale were compared using laser light scattering measurements. The most severely hydrotreated coal liquids have stability characteristics comparable to the jet fuels derived from petroleum and shale. Fuel degradation was monitored in the presence of added heteroatomic compounds. 2, 5-Dimethylpyrrole (DMP) is especially deleterious to fuel stability, promoting sediment formation and light scattering. Ageing of a SRC-II middle distillate is accelerated in the presence of Cu and O_2 as is evident from increase in viscosity and formation of pentane-insoluble components. FT i.r. spectra show that oxygen-containing compounds are concentrated in the pentane-insoluble fraction. Characterization of this ageing product by low-voltage high resolution mass spectrometry shows that it contains dimers, trimers, tetrameters, etc., of phenols. Experimental results lead to the conclusion that phenolic oxidative coupling reactions occur during ageing of SRC-II middle distillate.

A TIME-TEMPERATURE-CONCENTRATION MATRIX FOR SEDIMENT FORMATION OF ACTIVE SPECIES ADDED TO DIESEL FUEL

Robert N. Hazlett, John V. Cooney and Erna J. Beal

Accelerated fuel stability tests are important to the producers of fuels and to those performing research on the chemical phenomena involved in instability. In addressing this subject, the Naval Research Laboratory is defining the stability of diesel fuel containing added nitrogen compounds at several different temperatures. A complete matrix for production of insoluble material (filterable sediment plus adherent gum) has been developed for 43, 65 and 80°C temperatures, for time periods between 4 and 180 days, and a 10-fold concentration range of 2,5-dimethylpyrrole (DMP). A very regular pattern for insolubles formation has been found within this matrix. Insoluble material formed several times faster at 80°C compared to 43°C. Deposit formation rates were initially linear with time but decreased as the active species concentration declined. The rates exhibited a first order dependence on DMP concentration in the range of 45 to 450 parts per million of nitrogen. The sediment contained about 12% nitrogen and 18% oxygen irrespective of the temperature, time or DMP concentration conditions for the stability test. An energy of activation of 12 kcal/mole was calculated.

LONG TERM STORAGE STABILITIES OF OIL SHALE DERIVED FUELS

Nahum Por, Naphtali Brodsky and Rudolph Brauch

The development of technologies using sources other than conventional crude oils for production of liquid fuels is of primary importance. Oil shales are one of these alternative sources. The progress in developing technologies for liquid fuels production from oil shale is slow because of two considerations I The first is the relatively high cost of a barrel of shale oil derived from oil shales; the second is the quality of the shale oils. Much work is being done in this country by PAMA (Energy Resources Development) to develop suitable retorting processes the cost of which would not be prohibitive. The work reported here is a part of the endeavour to study the means for upgrading the shale oil and making it sufficiently stable either as a component in a blend with conventional crude oils or as shale oil fractions in blend with conventional crude oil fractions. This paper deals specifically with long term storage stabilities of blends composed of shale oil derived products with corresponding crude oil cuts. It is our pleasant duty to express our thanks to the Belter Energy Research Foundation who financed this study, the Israel Institute of Petroleum and Energy which made this work possible and the Oil Refineries Ltd, at whose Research Laboratories most of the experimental work had been carried out.

SESSION 4: MICROBIOLOGICAL ASPECTS IN LONG TERM STORAGE

SOURCES OF CONTAMINATION IN FUEL STORAGE TANKS ABOARD NAVAL SHIPS

Rex A. Neihof and Marian E. May

A survey has been made of sludges collected from fuel storage tanks on ships using water-compensated systems. To assess sources of particulate matter, samples were taken from more than eighty tanks on eight different ships and subjected to microscopic, chemical and microbiological analyses. There were considerable variations in the amount, quality and microbial content of the sludges in different tanks even on the same ship. Centrifugation separated the fuel and aqueous phases of the sludges and fractionated the particulates into sediment (sand, silt, microorganisms) and a low-density fraction (between water and fuel) consisting mainly of organic material typical of that found in unstable diesel fuels. Viable microorganisms were always found, but the dominant genera varied markedly in different samples. High counts of bacteria, including sulfate reducers, were associated with high aqueous pH (>7.8) and the presence of sulfide; a high content of yeast and fungi was correlated with 1 ow aqueous pH (< 4.0). Bacteria , yeast and fungi were found together at intermediate pH (4.0-7.8) in about half of the samples. Factors influencing microbial growth in fuel tanks are discussed. No samples contained detectable free hydrogen sulfide and, although substantial amounts of fungal debris were present in a few cases, the problem of microbiological contamination did not appear severe enough at present to justify the use of a biocide.

MICROBIAL PROBLEMS IN CONNECTION WITH LONG TERM STORAGE OF PETROLEUM PRODUCTS

R. Roffey, A. Norqvist and A. Edlund

Following the increased use of petroleum products during this century it has been observed that problems with corrosion and sludge formation have increased. It has also been found that the quail ty of stored petroleum products can be affected especially during long term storage. Research work has shown that some of these problems can be caused by microorganisms within the hydrocarbon bulk or at the interphase between hydrocarbon and water. In Sweden a large number of rock caverns for long term storage of different petroleum products have been constructed. These caverns are situated underground below the ground water table so that the water pressure keeps the oil in place. The storage system is based on the principle that petroleum products are stored on a water-bottom. During the last years some microbial problems have been observed in caverns where jet fuel and heating oil have been stored. It is the environmental situation; type of stored petroleum product and microbial activity that governs if problems will or will not appear. The limiting factors will be discussed. In this paper the mechanisms by which microorganisms can cause various problems during storage in rock caverns will be presented. Microbial investigations in caverns with problems will be discussed. Some microbiological and chemical methods developed in order to supervise the situation in rock caverns will also be presented.

METHODS TO INHIBIT HARMFUL MICROBIAL ACTIVITY DURING LONG TERM STORAGE OF JET FUELS IN ROCK CAVERNS

A Norqvist, R. Roffey and A. Edlund

In Sweden Jet fuel (JP4) has been stored underground in rock caverns during a number of years. The product is stored in rock caverns employing a fluctuating waterbed. Lately some problems have been observed in a few caverns in which the fuel has become corrosive. The corrosivity is caused by sulphate-reducing bacteria producing hydrogen sulphide from sulphate in the water bottoms of the caverns. The hydrogen sulphide passes through the water into the fuel making it corrosive. Analytical methods have been developed by which the inhibiting effect of different measures can be followed in caverns and laboratory systems. One way to test different inhibiting measures is to use model systems in the laboratory where the environmental situation in rock caverns can be imitated and the use of these will be discussed. The effect of different methods to inhibit the sulphate-reducing activity in laboratory systems and their applicability in rock caverns will be discussed.

MICROBIAL ASPECTS IN LONG TERM STORAGE OF HYDROCARBON FUELS

G. Miller and R. Fass

In this paper, microbial problems connected with long term storage of fuel distillates in above ground steel tanks and in models for unlined underground caverns will be discussed. The microbial contamination level of Jet fuel (MCL), stored in two types of above ground steel tanks, was surveyed over a long period. Results indicate that MCL depends on the tank design. Microbial sludge, with intensive activity of Sulfate reducing bacteria (SRB) and containing FeS, was found on the floor of several floating roof tanks. This sludge was formed due to poor drainage of water and to rust accumulation on the tank floor. Jet fuel, held in contact with FeS produced by SRB, became highly corrosive. Bench-scale storage experiments, simulating unlined underground caverns, were undertaken in order to assess the effect of microbial growth on the quality of Jet fuel and Diesel fuel. Results indicate that with sulfate containing brackish water, the most likely damage to be expected is corrosiveness of Jet fuel, caused by SRB. Diesel fuel was found to be less prone to such deterioration. Aerobic hydrocarbon utilizing bacteria and molds, which reduce the Redox potential and enrich the aqueous phase with suitable organic electron donors, prepare the ·conditions for SRB activity. A pilot plant, simulating the conditions at a site selected for rock caverns, was built from a block of sedimentary rock with brackish water as the confining agent. Jet fuel, stored for 30 months in this plant, remained intact.

SESSION 5: ABOVE AND UNDERGROUND STORAGE

UTILIZATION OF UNDERGROUND SPACE FOR THE STORAGE OF FUELS

Yaakov Vered-Weiss

In the late 1930's underground bulk storage for fuel was initiated for strategic and security purposes. The emphasis was on long term stocks and protection of quantity rather than quality. There were 2 main types natural caverns adapted or mined tunnels or shafts. These storages were either unlined or lined with cast concrete with or without steel plate lining. In some cases, discrete steel tanks were erected in excavations. The fuels stored were mainly marine fuels. Following World War 2 safe refined fuel storage were needed and there and then quality control became mandatory. Thereafter and at an accelerated pace after the world fuel crisis a number of underground storage systems were developed for the whole range of hydrocarbons.

FIELD EVALUATION OF STORAGE STABILITIES OF GASOLINE AND JET FUELS

David Luria

The stability of jet fuel is its property to withstand chemical changes. This property, as will be discussed later, relates to 3 subjects: 1) Storage at ambient temperatures; 2) Oxidation resistance under accelerated conditions; 3) Ability to withstand the degrading action of micro-organisms. Every one of these properties is affected by the j/f components and the ambience to which it is exposed. The most striking result of this instability is the chemical reactivity of some of the j/f components and the creation of deleterious products in the storage vessels, in the delivery systems, in the fuel systems and in the engine combustors. The discussion will cover three main topics: 1) Stability of j/f at moderate temperatures (up to 110 °F); 2) Stability of j/f at high temperatures for short periods of time; 3) Stability of j/f exposed to micro-organisms.