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EXECUTIVE SUMMARY

This discussion and data compilation relating to the storage stability of hydrocarbon liquids is divided into four principal sections: 1) background narrative, 2) references, 3) summary table, and 4) data tables.

The Background narrative section provides a general discussion of various types of storage stability tests arranged by type of sample involved. This generic review will provide an introduction for those new in the field or unsure of what data might be available. Approximately 150 references are cited in this section to aid in further investigation.

The second section is the References, consisting of an alphabetical listing of the literature cited along with an abstract for each entry. This section should provide additional details for anyone needing to use the data provided in the tables. Since many of the publications are difficult, if not impossible, to obtain today, these abstracts may have to suffice in place of the actual report.

The third section, or Summary Table, serves as a multientry index for the approximately 230 tables of raw data to follow. Information has been grouped according to the type of material involved, such as gasoline, diesel, jet fuel, coal liquid, etc. In addition, any compounds added are described along with the conditions under which the test was run. This should provide easy identification of data tables relevant to a particular investigation. References to original publications are provided so that more detail can be pursued.

The final section is made up entirely of Data Tables. These tables have all been retypeset for easier reading and rapid scanning. Formats have been changed from those in the original articles where it seemed it would help in understanding the data without access to the entire publication. This compilation is as complete as practical, and represents a broad spectrum of stability data.

In combination, these four sections should provide a ready reference source of data for those involved in the study of the storage stability of hydrocarbon liquids.

A REVIEW OF STORAGE STABILITY CHARACTERISTICS OF HYDROCARBON FUELS 1952 - 1982

by

J. W. Goetzinger,[1] C. J. Thompson,[2] and
D. W. Brinkman[3]

INTRODUCTION

With the increased sophistication of the modern engine the quality of fuels becomes of greater importance, and it is axiomatic that quality is interrelated to the stability or instability of the fuels. At the same time, trends toward lower quality fossil fuel feedstocks also increase the importance of understanding stability data and theory.

With the art and/or science of storage stability testing and evaluation evolving over the years into more acceptable and better understood procedures, a significant body of stability data has been accumulated. These data now permit a reasonably reliable prediction of stability at a number of conditions or temperatures based on measurements at one set of conditions.

In view of the long time frame for evolution of these data and the obscurity of some data, it seems advantageous to place in a single publication a summary of selected storage stability studies which are of scientific interest and value to the petroleum and related industries. An extensive literature review of storage stability was published in 1980 by Brinkman, et al (19)[4] citing some 264 references but providing no raw data. A similar review pertaining to jet fuel oxidation stability had been published previously by the Coordinating Research Council (26) in 1978.

DISCUSSION

Gasoline Storage Stability

Gasoline is a complex mixture of hydrocarbons containing small amounts of sulfur compounds and to a lesser degree nitrogen compounds. Often, during storage, these compounds react with the oxygen in the air and with one another to produce higher-molecular-weight materials commonly called gums. These gums are deleterious to fuel quality and tend to foul fuel lines, filters, valves and injection nozzles. For decades studies have been conducted in an effort to define the reactive compounds, the composition of the gums produced, and the mechanisms involved.

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1 Research Chemist, Department of Energy, Bartlesville Energy Technology Center, Bartlesville, Okla.
2 Consultant, Bartlesville, Okla. 74003.
3 Project Manager, Department of Energy, Bartlesville Energy Technology Center, Bartlesville, Okla.
4 Underlined numbers in parenthesis refer to references at the end of this report.

During the past 30 years, a number of studies have been directed to the development of improved and/or accelerated methods of gum formation, and even a greater number of analytical techniques have been investigated and applied in the identification of the gums so produced.

Experimental methods that utilize the generation of gums as a measure of stability have been developed and evaluated at ambient temperature (11), at 43° C (110° F) (6,10,80,96,100,102,120,121,122,126,132,133), at 60° C (140° F) (59), at 93° C (200° F) (98,99,102) and at 100° C (212° F) (62). Most of these methods were conducted at elevated temperatures to accelerate the deterioration of the fuel and thereby provide a means of short-term stability prediction. These tests included storage in sealed drums for 12 weeks to two years (11,59), in glass bottles (98,99), in a stirred autoclave under oxygen pressure (63), in aerated amber glass bottles (10), in stainless steel bombs (3,96), and in various other environments or conditions (7,102,104,135). Characterization of the gums has been accomplished using polarographic, infrared, NMR, chromatographic, distillation, mass spectral, reduction, and other techniques (7,101,123,124,125).

In a systematic study by Ward and Schwartz and augmented by the work of Whisman and Allbright, a series of some 22 papers was published describing samples, development of analytical techniques, and storage procedures (120). Many techniques were used in this extended study. Gasoline samples were separated into hydrocarbon types by adsorption and further separated by distillation (121,122). Then, the whole fuel and the fractions from chromatographic separation and distillation were tested for stability (122,124). The gasolines were subjected in a small part of this study to accelerated aging by ultraviolet light irradiation. The aromatic hydrocarbons and sulfur and nitrogen compounds which contributed to instability and gum formation at 110° F storage and during irradiation were investigated (105,125). Using another technique, a number of organic compounds were labeled with tritium, and these labeled compounds were added to gasoline samples to trace formation of gum in 43° C (110° F) storage. Measurement of radioactivity in the gum, by liquid scintillation counting, indicated whether or not the added compound had entered into the gum-forming reaction (99,104,126,127,128). Storage tests with some 70 tritium-labeled compounds suggested that the following compounds entered into fuel degradation processes in varying degrees: alkylbenzenes, cycloolefins, sulfur compounds, polycyclic compounds, diolefins and nitrogen compounds (4,129). Several carbon-14 labeled compounds and sulfur-35 labeled compounds were investigated (130) in addition to the tritium-labeled compounds. Radiotracer techniques also were used on synthetic gasoline-type mixtures (131), on residues formed in binary mixtures of pure compounds (132), on selected groups of hydrocarbons and sulfur compounds (133), and sulfur compounds and reactive hydrocarbons in n-heptane (100).

Cross correlation data between test methods and between a method and ambient storage are scarce.

A direct relationship or correlation between 16-hour, 93° C (200° F) storage and 43° C (110° F) storage for any period up to 32 weeks has been reported (2,97). Results of moderately accelerated tests for assessing storage stability compared with bulk storage over 2 to 14 years have been reported by Ruf (94).

LePera (68) determined autoxidation susceptibilities of 10 gasolines and two jet fuels as a measure of deterioration of petroleum products. The peroxide concentration-time curves revealed that autoxidation tendencies varied considerably.

Nixon (77) discussed oxidation of petroleum products, including reaction mechanisms, antioxidants and effects of oxidation on the properties of petroleum samples. Storage stability was discussed briefly in the context of oxidation during storage.

Samples of gasoline produced from coal, oil shale, and tar sands have been investigated for storage stability (12,20,33). Petroleum-derived fuels, stored under similar conditions, showed good storage stability, while most of the alternative fuels developed high levels of deposits after 32 weeks (12, 20).

Diesel Storage Stability

The properties of diesel fuels vary with the crude from which they are made and the processing to which they are subjected. Specification diesel fuels may have many and varying combinations of physical and chemical properties such as volatility, viscosity, ignition quality, cloud and flash points, Btu content and stability characteristics. The storage stability characteristics, or the relative chemical reactivity of the fuel in terms of its tendency to form degradation products which cause problems in storage and subsequently in distribution and combustion systems, is of principal concern in this discussion.

Stavinoha and Westbrook described 55 accelerated stability tests that have been applied to middle distillate fuels (109,110,111) and reported on the application and evaluation of a number of the methods. In related studies, the general topic of diesel fuel deterioration has been reviewed (108,112) including a consideration of fuel oxidation rates, test methods, and field problems.

The application of light scattering to diesel fuel stability studies has been reported (24,55). This method measures deterioration of diesel fuel by detecting the very small solid particles of gum while they are still suspended in the fuel. Other test methods of specific application to diesel fuels include predictive type tests for storage stability and compatibility of diesel fuel by MacDonald and Jones (73), "The Du Pont F21 149° C (300° F) Accelerated Stability Test" as reported by Henry (51) and the microscope cover slip technique of Worstell and co-workers (143).

The effects of container composition on diesel fuel storage stability has been investigated in work by Christian et al (24), MacDonald and Jones (73), and by LePera (69). Soft glass was reported to have a stabilizing effect on some unstable fuels.

Ritchie (92) investigated a variety of diesel fuels stored in steel tanks for periods up to 6 years. Comparisons were made between accelerated aging and 6-year ambient storage. Ruf (94) has reported correlations between

accelerated tests and long-term bulk storage. Stabilization of diesel fuels has been explored using oxygenated amines (61) as inhibitors and by caustic treating the fuel (90) to remove certain reactive species.

Four independent studies report research with the common objective of generating data of interest and value to the military establishment. Allbright, et al (1) evaluated storage stability of 41 Navy diesel fuel samples at 43° C (110° F) and tested 23 samples for compatibility with straight-run fuel during storage. LePera and Sonnenburg (70,71) investigated the storage of four fuels in 100-barrel steel tanks for periods up to 2 years. Bowden (10) in 1979 developed storage stability data on currently available fuels to serve as reference data, and Westbrook, et al (134) investigated the relative stability of neat fuel and fuel treated with additives in fully fueled vehicles in a humidity-controlled warehouse over a period of 30 months.

A number of storage stability studies have been conducted on diesel fuels derived from coal, oil shale and tar sands (9,14,18,21,28,39,41,53,93). These include studies on the effects of various nitrogen compounds on stability, consideration of the processing required to produce a stable fuel from shale oil, the factors that must be considered in converting from petroleum to syn-fuels, and the use of differential scanning calorimetry in stability studies.

Organic nitrogen compounds also have been evaluated for their tendencies to promote sediment in petroleum-derived diesel fuels during storage (39,143).

Jet Fuel Storage Stability

A systematic study by Whisman, et al (136,137,138,139) investigated the thermal and storage stability of many jet fuels using radiotracer techniques. Blends of jet fuel and carbon-14 labeled fuel components or additives were tested before and after storage. The use of radiotracers proved to be a very effective analytical tool in establishing the components involved in deposit or gum formation. During the course of this study, a significant body of data pertaining to thermal stability was also produced, but such data are outside the scope of this discussion.

The influence of selected nitrogen compounds (142) and organosulfur compounds (50) on storage stability of jet fuels has been reported. Parallel studies (30) using Lewis bases extracted from a syncrude were reported. The effects of compound class, basicity and steric hindrance were noted. Other studies (29,83,113) provided additional insight as to the effects of nitrogen compounds and coal liquid extracts on gum formation.

The effectiveness of a number of additives on storage stability of jet fuels has been reported (44,56,79). Some additives were effective in stabilizing the fuel, some had no measurable effect, whereas some had adverse effects on the oxidation stability.

Johnson, et al (54) provided a general discussion of storage stability including tests and factors affecting storage stability but included no data. Melent'eva, et al (74) compared stability of one fuel stored for 5 years at ambient conditions vs. 40-hour storage at 95° C. Other reported studies (78, 81,94) have investigated accelerated tests vs. long-term ambient storage, fuel deterioration after 30-weeks of storage at ambient conditions, and a correla-

tion of stability with composition of the fraction. Storage stability data on 10 commercially available fuels was determined to serve as reference data (10). Samples were stored in amber glass bottles for 4, 8, 16 and 32 weeks at 43° C (110° F) and then analyzed for soluble and insoluble gum.

The effect of storage on the thermal stability of fuels for high-speed aircraft was reported by Lander (67). The samples were stored in steel drums at ambient temperature for periods up to 18 months. Eight of 18 JP-6 fuels failed the test criteria after only 30 weeks of storage.

The effects on thermal stability of jet fuels resulting from their storage in typical ground-fuel-systems was investigated (57). The fuel was not degraded seriously by steels, aluminum or valve grease, but brass, bronze and butadiene-acrylonitrile rubbers of the type used in fuel hose produced serious degradation of fuel thermal stability.

Samples of jet fuels derived from coal, oil shale and tar sands have been investigated for storage stability (12,14,18,20,28,39,49,82,84,93). Several petroleum samples were included in the studies for comparison with synfuels. A variety of organic nitrogen, sulfur, and oxygen compounds were compared for their tendencies to promote gum formation in jet fuel under storage conditions.

Fuel Oil Storage Stability

A multiplicity of test methods (5,42,45,64,72,75,91,117,118) have been explored and described to estimate storage stability of distillate fuel oils. These include such specific tests as microscopic examination of the oil, light scattering, polarography, 3-year outdoor bottle and column storage, accelerated filter plugging, accelerated aging methods including a 1-day stability test, and other variations of time, temperature and conditions. Some correlation within a method appeared possible, but little correlation was noted among different methods.

A cooperative effort (103) between the Bureau of Mines and the Western Petroleum Refiners Association produced a series of reports summarizing storage stability data on distillate fuels that are representative of crude oil sources from major producing areas of the world. Straight-run fuels were the most stable; catalytically cracked fuels were intermediate in stability and thermally cracked were the least stable. Oxidation appeared to be a major factor in gum formation.

White (140), Clinkenbeard (25) and Nelson, et al (76) have provided a general discussion of distillate fuel storage stability. These studies addressed such points as the contribution of catalytically cracked stocks to fuel instability, effect of temperature on sediment formation, and how stability can be controlled or improved by proper processing.

Blending of straight-run and cracked fuels to provide distillate fuels has shown that some blends are incompatible resulting in gum deposits during storage, often in excessive amounts. Elmquist (34) investigated this problem and reported the effects of certain reactive compounds on stability, and Ward and Schwartz (119) suggested that storage stability of a blend could not be predicted from the storage stability of its components.

A Navy-CRC barge storage program (27) investigated the scale-up factor in going from bottle or drum to tank storage. Reasonable correlation was evident between bottle, drum and bulk storage at ambient temperature for soluble gum formation and light transmission but insoluble gum values from barge storage were much lower than bottle or drum, probably reflecting sampling difficulties.

The influence of sample container composition, metal vs. glass, was evaluated by Bentur, et al (8). Fuel oil was stored in vented metal cans and in vented glass bottles at ambient temperatures for 3, 6 or 9 months. All samples showed a continuous increase in color, acidity, and gum content with samples stored in metal containers producing more gum than those in glass, indicating a catalytic effect by the metal.

The effects of sulfur and nitrogen compounds on the stability of distillate fuel oils have been investigated (85,115). Such compounds as mercaptans, thiophenes, sulfides, pyrroles, indoles, pyridines and carbazoles represent a few of the many sulfur and nitrogen compounds studied. In a parallel study the effects of polar compounds in general were evaluated (31).

For many years additives have been suggested as effective in the reduction or prevention of deposit formation in both accelerated aging tests and in tank storage. A matrix of additives and test conditions was explored (32, 52) in determining the effectiveness of additives in preventing deterioration of distillate fuels during storage. Tetrahydropyrimidines (43) and hexahydropyrimidines (89) were reported as useful additives for gasoline and fuel oils (including diesel and jet fuel) to inhibit oil deterioration with its attendant formation of color and sludge. Other additives (65,66,144), whose exact structures were not reported, were claimed to inhibit sedimentation and retard discoloration in hydrocarbon fuels.

An explanation or mechanism for sediment formation in distillate fuels has been of interest to petroleum chemists for decades. Sauer, et al (95) and Buttrill, et al (23) conducted studies in an effort to determine the mechanism or mechanisms of deposit formation in such fuels. Certain compounds were suggested as inhibitors while others promoted gum formation under storage conditions.

Wiland (141) reported a statistical evaluation of storage stability using a mathematical method employing compositional data such as total sulfur and relative concentration values for atmospheric and vacuum resids.

Alternative or Synfuel Storage Stability

With the recognition that petroleum exists as a finite commodity and at the same time acknowledging commerce and industry's almost insatiable appetite for liquid fuels, synfuels from coal, oil shale and tar sands become of increasing importance. Gasoline, diesel and jet fuels derived from alternative sources have been discussed and cited in their respective sections of this report. Specific studies dealing with nonspecification or full boiling-range synfuels are now considered.

The storage stability of coal liquids from the SRC II process (106), the 1/2 ton/day Pittsburgh process (22), blends of SRC I and SRC II (46), liquids

from West Virginia coal by the Synthoil process (58), and hydropyrolysis liquids from South Africa (60) were investigated. Coal-derived liquids are so complex that it is difficult to define mechanisms, reactive compounds and methods to stabilize these materials. An electron spin resonance technique for the characterization of asphaltenes formed during aging of coal liquids has been described (35).

Brinkman (16) and Brinkman and Bowden (17) evaluated the storage stability of a variety of fuels and distillation cuts from petroleum and from coal, oil shale and tar sands. Most of these tests were conducted at 43° C (110° F) for periods up to 32 weeks. Hazlett, et al (48) aged crude shale oil at 50° C for 8-week periods. The authors suggested that fuel degradation during 1-year at ambient storage was not sufficiently serious to require alteration in processing.

Hazlett, et al (47) later investigated the mechanisms of syncrude/synfuel degradation and the effects of nitrogen compounds on the storage stability of middle distillates from Paraho crude shale oil. 2,5-Dimethylpyrrole was added to the fuel in concentrations from 45 to 450 ppm nitrogen, and the insolubles produced during storage were found to be directly proportional to the initial concentration of dimethylpyrrole.

Crude Oil Storage Stability

With the government's commitment to underground storage of hundreds of millions of barrels of crude oil, and to a lesser extent refined products, there is an increasing interest in the assessment of quality changes during such long-term storage. Three studies (15,19,107) in this area have addressed such points as: assessment of the state-of-the-art in underground storage; effects of storage on the quality of the stored fuel; development of a search file to enhance proper selection of crude oils to be stored; and an overall assessment of related problems. The investigations concluded that strategic storage of selected crude oil and products can be succcessfully accomplished in properly chosen sites.

Bowden and Lee (13) investigated the storage stability of six coal-derived liquids of various boiling ranges, three crude shale oils produced by different processes, and five hydrotreated shale oils. The stability of three petroleum referee fuels was also investigated, and the data were compared to the stability of the syncrudes.

Stability Studies in Pure Hydrocarbons

Frankenfeld and Taylor (36,37,38,40) in a systematic research effort using n-decane as the model fuel investigated the effects of nitrogen compounds and nitrogen compounds in combination with sulfur compounds, oxygen compounds or hydrocarbons on sediment formation. The authors noted that the quantity of sediment was much greater in samples stored under UV light than samples stored in darkness. They also noted that phenols reduced sediment formation, sulfides and hydrocarbons had little effect, and, although many nitrogen compounds were deleterious in fuel storage, some nitrogen compounds were not. Position of substituents on the pyrrole and indole molecules greatly influenced sediment formation; compounds with substituents in the 2 and 5 position were the most reactive.

Oswald (86,88) investigated the co-oxidation of olefins and mercaptans in pure hydrocarbons and suggested the formation of hydroperoxide intermediates as the mechanism for peroxidation and gum formation in untreated petroleum distillates. In a related study (87) using pure hydrocarbons as solvents, an effort was made to clarify the chemical reactions involved in color and sediment formation by pyrroles.

While a considerable body of storage stability data is available, there still exists a need for additional systematic studies. This report is intended to provide a point of reference for the generation of such needed data.

SUMMARY

This review of storage stability is divided into four main sections. The discussion or narrative section provides both background and state-of-the-art information in generic terms and cites 143 references.

The second section is the literature cited, consisting of 143 references, each with a supporting abstract.

The third section, and a most useful part of this review, is Table 1. This table provides a summary of data and cites 230 supporting tables and related references. For example, the materials being studied are grouped into categories such as Gasoline, Diesel, Jet, etc.; the storage media, if any, is reported, method of accelerating degradation, type of container, quantification technique and the specific tables and reference(s) which provide the detailed analytical data are cited. A review of Table 1 should significantly reduce the time required in a literature search.

The final section consists of 230 tables selected from the published literature on storage stability. Such a compilation, of necessity, is far from complete but is representative of a broad spectrum of recognized stability data.

This review article is intended to eliminate duplication of research efforts and to provide a concise referral source to scientists involved in stability studies.