

A COMPARISON OF LOW AND HIGH SULFUR MIDDLE DISTILLATE FUELS IN THE UNITED STATES

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ABSTRACT

Sixty-nine low sulfur (LS) and twenty-six high sulfur (HS) No. 2 diesel fuel samples were collected from twenty-four marketers throughout the United States in early 1994. Fuel samples were tested for chemical composition and stability. Statistical analysis of the data indicated that other than sulfur and nitrogen levels, the main compositional difference between LS and HS diesel fuels was a partial saturation of poly-aromatics to mono-aromatics in LS fuel. Storage stability via ASTM D4625 was improved in LS fuels compared to HS fuels. Hydroperoxide susceptibility of LS and HS fuels was equivalent and acceptable under conditions of ambient fuel transport and storage. However, under progressively severe thermal and oxidative stress, LS fuels appeared increasingly less stable than HS fuels.

INTRODUCTION

Before October 1993, No. 2 distillate fuel sold in the United States contained 0.2-0.4 % (wt) sulfur. As of October 1993, No. 2 distillate fuel used for on-highway vehicles was required to have a sulfur level no greater than 0.05 % (wt), i.e. 500 ppm (wt). This sulfur level reduction has been achieved by increasing the severity by which diesel fuel feedstocks are hydrotreated.

Limited data indicates that such low sulfur diesel fuels will have improved storage stability¹⁻³, i.e. form less sediment and dark-colored fuel-soluble materials. However, there have been concerns that resulting low sulfur diesel fuels may be more prone to form hydroperoxides upon storage.

The objective of the work reported in this paper was to compare the storage stability and hydroperoxide susceptibility of a large number of low and high sulfur No. 2 diesel fuels throughout the United States.

EXPERIMENTAL

Fuel Samples

Ninety-five No. 2 diesel fuel samples were collected during the period of February-March 1994. Sixty-nine samples were low sulfur (LS) diesel fuels; twenty-six were high sulfur (HS) fuels. Samples were collected in five geographic areas of the United States: Northern Midwest, Southern Midwest, Texas Gulf Coast, Rocky Mountains, and East Coast. Fuel samples spanned twenty-four marketers of diesel fuel, and were taken from both company-operated terminals and service stations. A few samples were taken directly from product pipelines. No attempt was made to determine if samples had been co-mingled during fungible pipeline shipment, or delivered segregated from the refinery. However, all samples represent diesel fuel being sold by the various marketers in the United States during early 1994.

All samples were shipped to the Amoco Research Center, Naperville, Illinois, by overnight express mail from the sampling points, and were stored at 40°F except when being tested.

Tests

Fuel samples were tested for chemical composition and stability using the following procedures:

Chemical Composition	Stability
Total Sulfur by Dispersive X-Ray Fluorescence (ASTM D4294)	Storage Stability (ASTM D4625) Initial Peroxide Number (ASTM D3703)
Total Nitrogen (ASTM D4629, modified) SMORS	Peroxide Number after ASTM D4625 (ASTM D3703)
Paraffins/Aromatics by Mass Spectrometry	Hydroperoxide Potential, CRC Procedure Hydroperoxide Potential, Oxygen Overpressure (OP) Procedure

Initial color (ASTM D1500) and ASTM D4625 final color were usually not determined for HS diesel fuel samples, since nearly all of those samples were dyed. The CRC Hydroperoxide Potential Procedure was originally developed for jet fuels⁶ and involves heating a 100 ml fuel sample at 65°C and 1 atmosphere air for four weeks. Peroxide number is then determined as an indication of the fuel's hydroperoxide susceptibility. The OP procedure for hydroperoxide potential was adapted from previously documented work involving jet fuels⁵. The procedure involves heating a 50 ml fuel sample at 100°C and 690 kPa (100 psia) O₂ for 24 hours. The peroxide number is then determined. The modification to the total nitrogen procedure was that the fuel sample was delivered to the combustion tube by a platinum boat rather than by standard syringe injection. SMORS (Soluble Macromolecular Oxidatively Reactive Species) are believed to be sediment precursors, and the procedure for measuring them has been previously documented⁶.

Statistical Treatment of Data

Data was statistically analyzed using SAS 6.08 for Windows. Statistical analysis was executed in three steps:

1. Distribution analysis
2. Analysis of geographic variance
3. Two sample t-testing of LS and HS fuels

Distribution analysis of the LS and HS results was done to ensure that normal distributions existed before running t-tests. When certain fuel test results gave non-normal distributions, a conversion to their logarithms usually gave the normal distributions required for valid t-testing. For a few tests, large numbers of zeros required the use of a non-parametric procedure known as the Median Scores test instead of the more commonly used t-test. Before t-tests were performed, the variance of data in each geographic area was analyzed to allow a stronger statistical treatment of the entire data pool. Two sample t-testing was then done to determine the statistical probability that a given mean test value was different for LS fuels compared to HS fuels. The confidence level (in percent) that the mean LS test value and mean HS test value is different was calculated. For the purposes of this paper, a difference in LS and HS mean test results was not considered statistically significant unless the confidence level was at least 90%. However, confidence levels that were somewhat lower were not entirely dismissed.

RESULTS AND DISCUSSION

Chemical Composition

Results of the statistical analysis of chemical composition tests are given in Table I. None of the LS fuels significantly exceeded the 500 ppm(wt) maximum allowed value for sulfur. Sulfur and nitrogen values reflected the already demonstrated fact² that hydrotreating removes sulfur-containing compounds more easily than nitrogen-containing compounds. Surprisingly, SMORS did not significantly decrease in LS fuels compared to HS fuels. The mass spectrometric data indicated that while LS fuels had more mono-aromatics and less poly-aromatics than HS fuels, they did not have significantly less total aromatics.

Stability

Results of the statistical analysis of stability tests are given in Table II. ASTM D4625 storage stability of all fuels was generally acceptable. LS fuel total insolubles averaged half that of HS fuel total insolubles, a statistically significant difference. This agrees with earlier work indicating that when diesel fuels are hydrotreated to reduce sulfur levels to less than 500 ppm(wt), conventional storage stability improves³. Dyeing practices prevented the determination of final color for the HS diesel fuels. However, the mean LS value (1.2, ASTM) appeared to be significantly improved from the typical HS values seen over the years in our laboratory. This also confirms previous observations that increased hydrotreating improves storage stability color, a significant result in view of the general inability of currently available additives to accomplish the same thing².

All fuels except one LS fuel gave zero initial hydroperoxides via the ASTM D3703 titrametric procedure. Previous researchers found the same result when examining field samples of HS diesel fuels. They concluded that HS diesel fuels were stable with respect to hydroperoxide formation³. Since the sixty-nine LS fuels in this study were also taken from the field, the same line of reasoning would indicate that LS diesel fuels are also stable with respect to hydroperoxide formation under commercial transport and storage conditions.

Differences in peroxide susceptibility between LS and HS diesel fuels varied directly with the severity of the sample storage conditions. Under ASTM D4625 conditions (13 weeks, 43°C, 1 atm. air), LS fuels developed hydroperoxide levels that were higher than HS fuels by a modestly significant amount (C. L. = 83.9%). Under the CRC conditions (4 weeks, 65°C, 1 atm. air), the same trend was observed, but the difference was very significant (C. L. = 99.2%). Under the OP conditions (24 hours, 100°C, 690 kPa O₂), the difference was even more significant (C. L. = 99.9%). It should also be noted that in all three hydroperoxide susceptibility tests, the mean final hydroperoxide level for LS fuels was far above the 1.0 meq O/Kg maximum level imposed on freshly refined JP-5 fuel. Hydroperoxide susceptibility for HS fuels exceeded this limit only for the most severe oxygen overpressure method.

The trend in hydroperoxide susceptibility is exactly what is expected, based on prior reported work and known chemical principles. Hydroperoxides in fuels are known to form via the well known peroxidation chain mechanism⁷. Very often, a slow initial stage of fuel oxidation, the induction period, occurs after which a more rapid rate of hydroperoxide formation is observed⁸. The length of the induction period will be determined by many factors including the level and efficacy of any naturally occurring or intentionally added antioxidants. Removal of those antioxidants by hydrotreating will reduce the induction period at any given set of incubation conditions (temperature, oxygen partial pressure, time). At very mild incubation conditions, the induction period may not be exceeded for most or all fuels. In that case, little or no difference in peroxidation susceptibility would be observed. As the incubation conditions become more severe, eventually the less stable fuels would exceed their induction period and rapid peroxidation would onset. These fuels would then be observed as more unstable. As the incubation conditions continue to become more severe, the separation of less stable and more stable fuels would become increasingly apparent up to a point.

Based on these observations, it appears that LS diesel fuels produced in the United States may be as hydroperoxide stable as HS diesel fuels under conditions they experience while getting to the end user. Also, results suggest that all three hydroperoxide susceptibility procedures used in this study may overpredict actual hydroperoxide levels generated by LS fuels under ambient conditions of fuel transport and storage. However, there is a real decrease in the peroxidation stability of LS diesel fuels compared to HS diesel fuels that could become apparent if the fuel is sufficiently stressed.

CONCLUSIONS

Major conclusions regarding the U.S. diesel fuels evaluated in this paper include the following:

1. Other than reduced sulfur and nitrogen content, the main statistically significant compositional difference between LS and HS diesel fuels was a partial saturation of poly-aromatics to mono-aromatics in LS fuels. There did not appear to be a strong statistical difference in total aromatics between LS and HS fuels.
2. Conventional storage stability as measured by ASTM D4625 was improved by a statistically significant amount in LS diesel fuels compared to HS diesel fuels. Both total insolubles and final color appeared to be improved.
3. Hydroperoxide susceptibility appeared to be equivalent and satisfactory for both LS and HS diesel fuels under the ambient conditions encountered during fuel transport and storage. However, under progressively severe thermal and oxidative stress, LS fuels appeared increasingly less stable than HS fuels.

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Table I
Results of the Statistical Analysis
Chemical Composition

Test	Low Sulfur Mean	Low Sulfur St Dv	High Sulfur Mean	High Sulfur St Dv	Conf. Level for Diff.	Test Metric ¹
Total Sulfur, ppm(wt)	296	92	2082	902	99.9	Log
Total Nitrogen, ppm(wt)	74.3	47.4	156.1	79.5	99.9	Original
SMORS, mg/100ml	.59	.50	.53	.35	35.4	Original
Mass Spectrometry Analysis, %(vol)						
Total Saturates	69.9	5.2	68.7	4.7	68.0	Original
Total Aromatics	30.1	5.2	31.3	4.7	68.0	Original
Mono-Aromatics	23.9	4.4	19.6	3.4	99.9	Original
Poly-Aromatics	6.3	2.2	11.7	3.3	99.9	Original

1. Test Metric indicates whether original data or natural logarithms were used to generate statistical information. See EXPERIMENTAL section for more information.

Table II
Results of the Statistical Analysis
Stability

Test	Low Sulfur Mean	Low Sulfur St Dv	High Sulfur Mean	High Sulfur St Dv	Conf. Level for Diff.	Test Metric ¹
Storage Stability, ASTM D4625						
Total Insolubles, mg/100ml	.30	.31	.67	.67	99.9	Log
Final Color, ASTM	1.20	.514	.750 ²	--	--	Log
Hydroperoxide Analysis, meq O/Kg						
Initial Peroxide Number, ASTM D3703	.071 ⁴	.590	0.00	0.00	--	Original
Peroxide Number after ASTM D4625 ³	21.3	156.0	.78	1.42	83.9	Original
Hydroperoxide Potential, CRC ³	23.6	131.3	.10	.53	99.2	Original
Hydroperoxide Potential, OP	339	545	19.8	11.2	99.9	Log

1. Test Metric indicates whether original data or natural logarithms were used to generate statistical information. See EXPERIMENTAL section for more information.

2. High sulfur results based on 1 observation

3. Because of the large number of zeros, the Median Scores test results are reported

4. Only one of the sixty-nine LS fuel samples had a non-zero result.