

# EFFECT OF INCREASINGLY SEVERE HYDROTREATING ON STABILITY-RELATED PROPERTIES OF NO. 2 DIESEL FUEL

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## ABSTRACT

This paper reports the effect of increasingly severe hydrotreating on the compositional and stability-related properties of four No. 2 diesel fuels ranging in sulfur level from 222 ppm to 11 ppm. Denitrification was essentially complete when the fuel sulfur level had been reduced to 86 ppm. At 222 ppm sulfur (similar to current U.S. low sulfur diesel fuels), fewer multi-ring but similar total aromatics were present compared with the high sulfur feed. With further sulfur removal, total aromatics were reduced as well, due to removal of mono-ring aromatics. Storage stability was excellent for all four fuels. Hydroperoxide susceptibility appeared adequate to excellent under conditions similar to commercial transport and storage. Additional information concerning diesel fuel instability chemistry was also demonstrated.

## 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 early data indicated that such low sulfur diesel fuels would have improved storage stability,<sup>1-3</sup> i.e. form less sediment and dark-colored fuel-soluble materials. A more recent study verified this conclusion.<sup>4</sup>

A few studies have been published to date concerning the effect of hydrotreating on No. 2 diesel fuel peroxidation tendency.<sup>7-8</sup> The most significant and most recent study indicated that commercial U.S. low sulfur diesel fuels did have increased hydroperoxide susceptibility compared with commercial U.S. high sulfur diesel fuels under sufficiently accelerated conditions. However, no such tendency was observed under ordinary field conditions of fuel transport and storage.<sup>4</sup>

The primary objective of the work reported in this paper was to evaluate an already available set of four hydrotreated No. 2 diesel fuels made from the same feedstock. Since finished fuel sulfur levels began at 222 ppm and went as low as 11 ppm, trends in fuel properties as a function of hydrotreating severity could be examined. Resulting data could provide useful insight not possible by looking only at commercial U.S. low sulfur (LS) and high sulfur (HS) diesel fuels. Also, the data could provide important information for future U.S. diesel fuel production, which might be required to attain even lower sulfur levels

## EXPERIMENTAL

### Fuel Samples

Each of the four No. 2 diesel fuel samples used in this work was obtained by a two-stage hydrotreating of a highly aromatic feedstock having the following gross compositional properties as measured by mass spectrometry:

Aromatics, %(wt)	
Total	46.5
Mono	17.6
Di	23.5
Tri	2.9

Stage	First*	Second
Catalyst	Co/Mo	Pt/Pd on Mol Sieve
Psig H2	500	900
lhsv	2.1	1.0
Temperature, °F	650	500-550
H2-Circulation Rate, scf/bbl	1,500	5,000

The samples were about one year old when testing began. During that year, they had been stored in clear, sealed glass bottles at ambient laboratory temperature.

## Tests

The four additive-free fuel samples were tested for chemical composition and stability using the following procedures:

### Chemical Composition

Total Sulfur by Dispersive X-Ray  
Fluorescence (ASTM D4294)  
Total Nitrogen (ASTM D4629, modified)  
Basic Nitrogen (ASTM D2896)  
SMORS  
Phenalenones  
Aromatics by Mass Spectrometry

### Stability

Oxidative Stability (ASTM D2274)  
Nalco Pad Stability  
Storage Stability (ASTM D4625)  
40-Hour Stability  
Initial Peroxide Number  
(ASTM D3703)  
Peroxide Number after  
ASTM D4625 (ASTM D3703)  
Hydroperoxide Potential,  
CRC Procedure  
Hydroperoxide Potential, Oxygen  
Overpressure (OP) Procedure

The ASTM procedures are well documented and will not be described further here. The Nalco Pad stability procedure measures thermal stability and has been described elsewhere.<sup>5</sup> ASTM D2274 and the Nalco Pad test are known not to correlate with real storage stability. However, they were included since they continue to be used as specification tests by many diesel fuel marketers and customers. The 40-Hour Stability test is a procedure developed and used by Amoco Oil Company and has been shown to correlate well with the reliable ASTM D4625. During this test, a 350 ml sample of distillate fuel is stressed at 80°C for 40 hours in a mineral oil bath while oxygen is bubbled through the sample at a rate of 3 liters/hour. The sample is then removed from the oil bath and allowed to cool for two hours in the dark. After determining the final color, the sample is diluted to 1, 225 ml with N-pentane, mixed thoroughly, and filtered through a tared 0.8 micron filter. After rinsing with N-pentane, the filter is dried and weighed to determine the total insolubles. Initial Peroxide Number should actually be regarded as a Peroxide Potential (susceptibility) test with a one year, ambient temperature storage period. The CRC Hydroperoxide Potential procedure was originally developed for jet fuels<sup>6</sup> 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 fuels.<sup>7</sup> The procedure involves heating a 50 ml fuel sample at 100°C and 690 kPa (100 psia O<sub>2</sub>) 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 documented.<sup>8</sup> Phenalenones are believed to be SMORS and sediment precursors, and the analytical method for measuring them was based on a previously reported procedure.<sup>9</sup>

## RESULTS AND DISCUSSION

### Chemical Composition

Chemical composition test results are given in Table I. Total and basic nitrogen levels dropped significantly as the fuel was hydrotreated from 222 ppm to 86 ppm sulfur. Further reductions in sulfur did not result in much further decrease in nitrogen levels. No phenalenones were detected in any of the four hydrotreated diesel fuels. Since phenalenones are formed by the facile oxidation of phenalene, this indicates that the hydrotreating process was probably severe enough to reduce all phenalenes that may have been present in the original feed. Only the 222 ppm sulfur fuel had a high level of SMORS. The other three fuels had SMORS that were similar to the mean values of both LS and HS commercial U.S. diesel fuels.<sup>4</sup> This indicates that by hydrotreating the feed to 86 ppm sulfur, SMORS precursors were nearly removed. Since phenalenones are believed to be SMORS precursors, the absence of phenalenones and the high SMORS level in the 222 ppm sulfur fuel is interesting. It implies that either phenalenones initially present in the feed were not removed by hydrotreating and then completely reacted to form SMORS during the one year storage, or else the SMORS formed in the 222 ppm sulfur fuel were formed from precursors other than phenalenones. As will be shown in the subsequent section on stability, the latter explanation is the more likely one.

Gross hydrocarbon analysis indicated that the main change in going from the feed to the 222 ppm sulfur fuel was to reduce polycyclic aromatics to monocyclic aromatics, with no overall reduction in aromatic content. This is consistent with earlier U.S. commercial diesel fuel survey data.<sup>4</sup> However, as hydrotreating became progressively severe, both poly- and mono-cyclic aromatics significantly decreased.

### Stability

Stability test results are given in Table II. All four samples showed excellent thermal and storage stability. As sulfur level decreased, overall results remained constant.

SMORS measured on the filtered samples after D4625 storage showed a decreasing trend with decreasing sulfur level. Only the 222 ppm sulfur and 86 ppm sulfur fuels developed significant additional SMORS relative to the amounts initially present. The 222 ppm sulfur fuel developed a quite high level of SMORS. Since all four fuels prior to D4625 testing contained no measurable phenalenones, the SMORS developed during D4625 testing must have been formed from other precursors. Also, since ASTM color did not darken much during D4625 testing, the SMORS formed must not have been very dark. This is in contrast to HS diesel fuel, where previous work indicates that SMORS contribute to aged color formation<sup>4</sup> and can correlate to aged sediment formation.<sup>10</sup> The major implication of this result is that SMORS formed in LS diesel fuel are different from SMORS formed in HS diesel fuel. In fact, the SMORS formed in HS diesel fuel may include a wide range of compounds beyond the indolyl phenalenes and indolyl phenalenones typically suggested in the literature.<sup>11</sup> This wide range of compounds may include some of the SMORS formed in LS diesel fuels. Although not published, some of these conclusions concerning the diversity of SMORS in diesel fuel have been suggested by one of the researchers who first discovered SMORS.<sup>12</sup>

Hydroperoxide susceptibility of the four progressively hydrotreated fuels was profiled by measuring the peroxide number developed after four increasingly severe storage conditions. Based on the one year ambient data, it appears that "real world" hydroperoxide susceptibility of U.S. LS diesel fuel will improve as sulfur levels are further reduced beyond the current typical levels. Although the 7 meq O/Kg value for the 222 ppm sulfur fuel is within the "problem" range cited in prior jet fuel literature, it is unlikely that much on-highway diesel fuel will be stored for one year. Previous data indicated that commercial U.S. LS fuel (with similar sulfur levels) gave negligible levels of hydroperoxides.<sup>4</sup> Those fuels represented what the end user would likely receive. Whatever level of hydroperoxide stability exists in today's LS diesel fuel, further reductions in required sulfur levels should improve that stability.

Looking at the entire peroxide number data, an interesting trend can be seen. As test storage conditions increased in severity, the maximum peroxide number observed among the four fuels shifted towards lower sulfur diesel fuel. For instance, the initial peroxide number (after one year storage in the laboratory) showed the highest level in the 222 ppm sulfur fuel. A similar pattern was observed for peroxides measured after D4625 storage (43°C, 13 weeks, 1 atm. air), although overall values after D4625 were higher than the initial values. However, after the even more severe CRC conditions (65°C, 4 weeks, 1 atm air), the maximum peroxide level shifted towards the 86 ppm sulfur fuel. After the most severe OP storage condition (100°C, 24 hours, 690 kPa O<sub>2</sub>), the maximum peroxide number was observed in the 39 ppm sulfur fuel, with much lower values for the other three fuels. These test results can be best understood by remembering that a fuel's peroxide number reflects the difference between the rates of two processes: hydroperoxide formation and hydroperoxide decomposition. Factors promoting hydroperoxide formation are apparently more important under the less severe test storage conditions. One such factor is the concentration of compounds most prone to hydroperoxide formation. As indicated previously,<sup>4</sup> compounds containing benzylic carbon are among the most prone to hydroperoxide formation. As poly-cyclic aromatics are reduced to mono-cyclic aromatics with total aromatic content remaining constant, benzylic carbon content increases. This fact has been proposed as a primary reason why hydroperoxide susceptibility under accelerated conditions is greater in commercial LS diesel fuels compared with HS diesel fuels.<sup>4</sup> However, when hydrotreating is severe enough to reduce all aromatic species, benzylic carbon content will decrease, replaced by carbons less susceptible to hydroperoxide formation. This would explain why peroxide number decreased under lower test severity as the fuel was more severely hydrotreated.

However, as test storage conditions become more severe, factors promoting hydroperoxide decomposition apparently become more important for the less hydrotreated diesel fuels. One factor that may contribute to this effect is the concentration of naturally occurring hydroperoxide decomposers in the fuels. These compounds are removed as the fuel is progressively

hydrotreated. So, at higher test severity, hydroperoxide decomposition by naturally occurring hydroperoxide decomposers will be greater in the less hydrotreated diesel fuels. Also, there is some evidence that benzylic hydroperoxides are somewhat less kinetically stable compared with non-aromatic hydroperoxides. If so, this would also tend to increase the rate of hydroperoxide decomposition in the less hydrotreated diesel fuels.

More data will be required to fully explain how these and other factors contribute to the peroxide number trends evident in the Table II data.

It is interesting to note that the most severely hydrotreated diesel fuel (11 ppm sulfur) gave only about 0.5 meq O/Kg for all test storage conditions. Without further analysis for final oxidation products, it can only be concluded that for that fuel the rates of hydroperoxide formation and decomposition were nearly equal under all test storage conditions.

## CONCLUSIONS

The work reported in this paper supports the following conclusions:

1. Current U.S. commercial LS diesel fuel has less multi-ring aromatics than HS diesel fuel, but similar total aromatic levels. With further hydrotreating, total aromatics are reduced as well, due to removal of mono-ring aromatics.
2. As diesel fuels are hydrotreated to and beyond current U.S. commercial LS diesel fuel sulfur levels, storage stability remains excellent.
3. As diesel fuels are hydrotreated to current U.S. commercial LS diesel fuel sulfur levels, hydroperoxide susceptibility remains acceptable under normal conditions of commercial transport and storage. As diesel fuels are further hydrotreated, hydroperoxide susceptibility under those same conditions should improve.
4. SMORS in non-additized LS diesel fuel do not significantly contribute to color darkening. Neither are they sediment precursors. LS diesel fuel SMORS are either chemically distinct from HS diesel fuel SMORS, or they are an innocuous subset of HS diesel fuel SMORS.

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**TABLE I**  
**CHEMICAL COMPOSITION**

Sulfur, ppm (wt)	222	86	39	11
Total Nitrogen, ppm (wt)	75	8	4	<1
Basic Nitrogen, ppm (wt)	12	<5	<5	<5
SMORS, mg/100 ml	2.5	0.4	0.4	0.2
Phenalenones, ppm (wt)	ND <sup>1</sup>	ND <sup>1</sup>	ND <sup>1</sup>	ND <sup>1</sup>
Aromatics by Mass Spec., % (wt)				
Total	53	28	13	7.2
Mono-cyclic	43	24	11	5.3
Di-cyclic	9.7	3.3	1.1	0.8
Tri-cyclic	0.6	0.7	0.9	1.0

<sup>1</sup> Not detected

**TABLE II**  
**STABILITY**

Sulfur, ppm (wt)	222	86	39	11
Initial Color, ASTM <sup>1</sup>	<1.5	-6 <sup>2</sup>	-16 <sup>2</sup>	<1.0
Stability, D2274				
Total Insolubles, mg/100 ml	0.2	0.1	0.0	0.0
Final Color, ASTM	<2.0	<0.5	<0.5	<1.0
Nalco Pad Rating	1	1	1	1
40-Hour Stability				
Total Insolubles, mg/100 ml	0.4	0.1	0.0	0.0
Final Color, ASTM	<1.5	-6 <sup>2</sup>	-16 <sup>2</sup>	<1.0
Stability, D4625				
Total Insolubles, mg/100 ml	0.3	0.2	0.2	0.2
Final Color, ASTM	<2.0	<0.5	0.5	<1.0
SMORS, mg/100 ml				
Initial <sup>3</sup>	2.5	0.4	0.2	0.2
After D4625	11.0	1.0	0.4	0.3
Hydroperoxide Potential, ineq O/Kg				
Initial <sup>4</sup>	7.6	1.7	0.43	0.50
After D4625	193	24	1.4	0.55
CRC <sup>4</sup>	26	28	2.0	0.43
OP <sup>5</sup>	1.3	21	199	0.68

<sup>1</sup> ASTM D1500 except where noted

<sup>2</sup> Saybolt color

<sup>3</sup> Measured on fuels after 1 year ambient laboratory temperature storage

<sup>4</sup> CRC Hydroperoxide Potential Method as described in EXPERIMENTAL section

<sup>5</sup> Oxygen Overpressure Method as described in EXPERIMENTAL section