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THE EFFECT OF ALIPHATIC OLEFINS ON THE STABILITY OF DIESEL FUEL.

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ABSTRACT

The effect of aliphatic olefins on the storage stability of a number of distillates was observed and characterised, mainly by determining the amounts of total insolubles formed during accelerated ageing.

It was observed that the aliphatic olefins in light cycle oil (LCO), a product of catalytic cracking, accelerated the degradation process in accordance with general expectations and in straight run diesel (SRD) and hydrotreated diesel (HTD), aliphatic olefins were shown to have no effect on stability. However, contrary to expectations, the aliphatic olefins inhibited the degradation process of light waxy gas oil (LWGO).

The effect of aliphatic isomers on the degradation of LCO is in the order of terminal olefins < internal olefins < branched chain olefins. The effect of aliphatic olefinic isomers on LWGO is, on the other hand, in the order of terminal olefin > internal olefins > branched chain olefins.

Three possible mechanisms to explain the effect of aliphatic olefins on the LCO and LWGO samples are proposed.

INTRODUCTION

Diesel fuel is a highly complex hydrocarbon product, boiling between approximately 150° C and 400° C. The world-wide increase in demand for middle distillate fuels (jet fuels and diesels) has been greater than that for any other petroleum product[1]. Refineries have met this demand partly by increasing the boiling range of components added to the middle distillate fuels to the maximum allowed by pour point requirements, and partly by cracking heavier distillates. A component of the distilled cracked stock, light cycle oil (LCO), may be added directly to automotive diesel fuel.

The availability and quality of crude oil as refinery feedstock[2] is decreasing worldwide. This reduction in feedstock quality must effect the chemical composition of the refinery products, necessitating an increase in the range of the components blended to diesel and other fuels if product quality is to be maintained. As the quality of the feed stock has decreased, the number of reports of filter blockage and engine malfunction caused by the formation of sediment in the fuel has increased[3]. Studies have confirmed that unstable diesel fuels will produce sediment on storage and that the amount of sediment may be related to the presence of un-hydrogenated LCO in the fuel[4]. Hydrogenation of the LCO prior to its addition to diesel fuel will remove most of its sediment producing tendency, but this procedure adds to the refining costs.

Development of undesirable properties such as sediment, peroxide, and colour formation involves complex physical and chemical processes[5]. Both the detailed composition of the fuel and the environment to which the fuel is exposed, play a major role in these processes. Formation of sediment and gum in middle distillates was primarily the result of three separate reactions[6]:

(1) acid-base reactions where the organic acids react with basic nitrogen to produce sediment,

(2) oxidative gum reactions where olefins react with oxygen to produce gum and

(3) esterification reactions where aromatic hydrocarbon and heterocyclic nitrogen compounds, together with benzothiols, react in a multi-step process to produce sediment.

Studies of the correlation of hydrocarbon composition with instability indicate that the stability decreases in the order of paraffins, naphthenes, aromatics and olefins[7]. Olefins present in the distillate fuels result either from the direct application of heat to petroleum in the course of refining, or from thermally or catalytically cracked products blended to the fuels. The amount of olefins in a straight run diesel (SRD) and light cycle oil (LCO) is generally less than 0.1% and 3.0% respectively[8]. Terminal olefins, internal olefins and branched chain olefins were observed to have different rates of instability in aged oil shale samples[9]. The structures of the olefins and their ease of oxidation may have a considerable effect on the rate of the gum or sediment formation. The chemical reactivities of the terminal, internal *cis,* internal *trans* and branched chain olefins will no doubt differ, although as yet there are no reliable data to prove this reasonable assumption.

EXPERIMENTAL

Ageing method

The method for ageing oil samples was adapted from the work of Jones *et al.*[10] and Bahn *et al.*[11] The ageing of the oil was carried out on a 50 mL aliquot of sample in a 100 mL pyrex bottle or on a 100 mL of sample in a 250 mL pyrex bottle. The pyrex bottles used were wrapped in aluminium foil, sealed with teflon liners and capped with tight fitting plastic screw-on lids. The oil sample was suction filtered using a 0.45 μ PTFE filter and saturated with oxygen.

Total Insolubles

The following method for determination of the total insolubles formed in the aged fuel was adapted from ASTM D2274-88 and the work of Bahn *et al.*[11] The insoluble particulates were filtered through a 0.45 μ PTFE filter. The adherence in the bottle was dissolved in 3 x 5 mL portions of 1:1:1 toluene-acetone-methanol (TAM) and transferred into a 20 mL scintillation glass vial wrapped with aluminium foil. The TAM solvent was evaporated at 40° C under a gentle flow of nitrogen. The weight of total insolubles formed is the sum of weights of insoluble particulates and adherence.

Existent soluble gum

The method for soluble gum determination was adapted from ASTM D381-86 and from the work of Beranek *et al.*[12] Evaporation at 240° C was extended for a further seven minutes after the time when there was no more smoke observed coming from the heated oil sample. The value of the soluble gum was reported as g/100 mL, or where necessary per available volume of sample.

Diesel Fuels

Diesel fuels, such as straight run diesel (SRD), automotive diesel fuel (ADO), hydrotreated diesel (HTD), light cycle oil (LCO) and light waxy gas oil (LWGO) in this study were obtained directly from a modern, major Australian refinery.

Olefins

Mixtures of olefinic model compounds were made up using C_{12}, C_{14}, C_{16}, C_{18} and C_{20} olefins in the proportion of 1.0 : 2.0 : 2.6 : 1.5 : 1.1. Terminal olefins were obtained from Aldrich Chemical Company and used directly. The internal and branched chain olefins were isomerised from these terminal olefins using double bond shift and skeletal shift isomerisation respectively by passing them over kaolinite, 36 to 52 mesh, at temperatures in the range 160 to 250° C and 330 to 350° C. The internal model compounds consist mainly of internal-2 and internal-3, together with a lesser amount of internal-4 up to internal-9 isomers. The branched chain model compounds are comprised mainly of terminal branched chain isomers with some internal branched chains.

RESULTS AND DISCUSSION

Ageing of stable diesel samples such as SRD, ADO and HTD for periods up to 14 days at 80° C does not affect the amount of the total insolubles, but it does affect markedly the total insolubles of the moderately unstable diesel oil such as LWGO, or the unstable diesel oil such as LCO (Table 1).

The total amounts of the insolubles and adherence correlate well with time (Figure 1). The linear regression coefficients (r) of 0.9970 and 0.9977 were obtained for LCO and LWGO respectively. The slope of the linear regression, which indicates the rate of the formation of the total insolubles, is about 0.00092 ± 0.00003 g/100 mL per day for LCO and about 0.00057 ± 0.00003 g/100 mL per day for LWGO.

The ideal diesel oil sample for the study of the effect of olefinic isomers on the stability of the diesel oil is an oil which inherently contains considerable amounts of olefins. LCO contains olefins at concentrations from three to five percent, but also contains nitrogen, sulfur and oxygen compounds. LCO is not a stable oil, but the presence of these heteroatomic compounds, together with the olefins, makes it difficult to determine to what extent the olefins alone degrade the oil. Therefore, to know the extent of the degradation effect of the olefinic isomers on the stability of diesel oil samples, a mixture of olefinic model compounds was doped into a less complicated sample. SRD and LWGO, representing the base of light diesel and heavy diesel oil respectively were used in this role.

Table 2 shows the effects of the terminal, internal and branched chain olefins on LCO samples aged at 80° C for 31 days. The addition of olefinic isomers at concentrations of 3 weight percent increases the LCO instability. This is a general phenomenon in cracked diesel oil[13]. The data shows that branched olefins are more deleterious than internal olefins, which in turn are more deleterious than terminal olefins. Fookes *et al.*[9] in their study on the stabilities of shale oils, also found that branched olefins are more deleterious than internal olefins, which are in turn more deleterious than terminal olefins.

The effect of olefinic isomers on SRD and LWGO

Table 3 shows that the addition of terminal olefins at concentrations of up to 6 weight percent to SRD does not show any significant effects on the stability of the aged SRD. This may be because the SRD diesel fuel is so stable that a 7 days period of ageing at 80° C is not sufficient to show the effects of the addition of the terminal olefins. However, the addition of terminal olefins at concentration of up to 6 weight percent to moderately unstable LWGO on the other hands is surprising. Contrary to the observation of the effect of terminal olefins on LCO and the common assumption in the literature, the data shows that the stability of the aged LWGO doped with terminal olefins seems to be better than the stability of the aged blank LWGO. Prolongation of the ageing time on LWGO samples to 14 days also showed the same result.

Tables 4, 5 and 6 show that, relative to the amount of total insolubles on aged LWGO samples, the effect of the internal olefins to stabilise the aged samples is less than that of the stabilising effect of terminal olefins. The branched chain olefins seem not to have any stabilising effect on the aged LWGO at all. While the terminal olefins brings about an increase in stability in LWGO, the addition of internal and branched olefins does not cause any degradation effect on the LWGO.

The very significant differences observed between the blank aged LWGO, the terminal, the internal and the branched chain olefins doped LWGO's, is the amount of existent soluble gum produced. The amount of the soluble gum produced by the internal olefins is about three to six times higher than that produced by the blank aged LWGO and that produced by the terminal and branched chain olefins.

Confirmation of the effect of olefinic isomers on LWGO and LCO

Because of the contradictory effects of olefinic isomers on the stabilities of LCO, on LWGO observed in this study and especially to confirm the findings on LWGO, a series of experiments was then carried out using a greatly extended ageing period. Because the properties of the insolubles of the LWGO made the filtration of the 100 mL samples used in the initial experiments through the 0.45 μ nylon filters very slow (about 2 hours), 50 mL batch samples were used instead. The results of these confirmatory experiments, which were conducted in triplicate, are listed in Tables 7 and 8.

I. Independent t-Test

An independent t-Test for the total insoluble properties was performed on the blank and the doped samples both for LCO and LWGO. From the results in Table 7, with N Equal to 3, at the 0.05 confidence level, it can be seen that the two means of the blank and terminal olefin doped LCO samples are not significantly different. The blank and internal olefin doped LCO samples are significantly different and the blank and branched chain olefin doped LCO samples are significantly different. These results indicate that the addition of terminal olefins to LCO does not really degrade the storage stability of the LCO, but the addition of internal olefins and the addition of the branched chain olefins cause degradation of the storage stability of LCO. The olefinic isomers degrade the stability of the LCO samples in the order of terminal < internal < branched chain olefins.

The data in Table 8, at the 0.05 confidence level, confirm that the two means of the blank and terminal olefin doped LWGO samples are significantly different. The blank and internal olefin doped LWGO samples are significantly different and the blank and branched chain olefins doped LWGO samples are not significantly different. These findings show that the addition of terminal olefins and internal olefins to LWGO increases its storage stability, but the addition of branch olefins does not increase stability. The olefinic isomers stabilise the storage stability of the LWGO in the order of terminal > internal > branched chain olefins.

Both the two t-Tests on the effects of the addition of terminal olefins on LCO and LWGO indicate significant effects on the total insoluble properties of the aged samples, but in different ways. While the addition of the terminal olefins to LCO degrades the oil, the addition of the same terminal olefins to LWGO improves the stability of the oil.

II. Extending the addition of terminal olefins to LWGO

To determine the consistency of the effects of the terminal olefins in stabilising the LWGO samples, a series of ageing experiments using terminal olefins doped into LWGO at concentrations of up to 9% was carried out. The results are shown in Table 9. All experiments were carried out in triplicate and the results analysed using the Student t-Test at the 0.05 confidence level. It can be seen that the two means of the blank and the 1.5% terminal olefin doped LWGO samples are not significantly different. The blank and the 3, 6 and 9% terminal olefin doped LWGO samples are significantly different.

The effect of olefinic isomers on soluble gum.

It was observed earlier that the aged samples doped with internal olefins produced more soluble existent gum than the blank or the samples doped with terminal olefins. The levels of soluble existent gum is determined by evaporating the samples at 240° C while blowing them with hot nitrogen at a rate of about 3L/minute, until no more smoke comes out from the gum. To ensure that the soluble existent gum in the aged olefin doped samples is really formed during the ageing period and not because of the effects of the heat during the execution of the soluble gum test, a set of soluble existent gum test was carried out on both doped fresh diesel which was not aged and doped diesel fuel samples which were aged. The results are shown in Table 10.

The data shows that blank LWGO and the olefin doped LWGO for both the aged samples and the fresh samples had the same trend; the internal olefin doped LWGO produces more soluble gum compared with that of the blank LWGO or the terminal and branched chain olefin doped LWGO by about three to six fold. The isolated soluble gum of the samples doped with internal olefins was a very viscous black liquid.

The above observations suggest that for internal olefin doped diesel fuel samples, the amount of soluble gum produced has nothing to do with the chemical or physical processes occurring during the ageing of the samples, but results from the effects of the heating (about 240° C) given to the samples during the execution of the soluble existent gum test.

The effects of the addition of SRD to LCO and LWGO

Some authors[14,15] reported that the addition of stable diesels, such as straight run, to unstable diesel LCO would improve the stability of the LCO. The olefinic model compounds used for doping in this experiment have lower specific gravity than that of the doped LCO and LWGO samples. To check that the stability effect experienced by the LWGO samples does not occur because of the dilution factor due to the addition of the lighter olefinic model compounds, a series of ageing studies was carried out on LCO and LWCO samples using light, stable SRD as a dopant. The results are shown in Table 11. The data shows that the addition of 3% SRD to LCO does not bring about any effect on the stability of the LCO. The addition of the SRD to LWGO at concentrations of up to 6% also does not bring about any stabilising effect on the LWGO.

The effect of olefinic isomers in the formation of total insolubles in LCO and LWGO

Based on the data for the total insolubles in LCO and LWGO there are several mechanisms possible to explain the effect of olefins on the stability of oil samples. Individual reaction mechanisms will depend on the type of the reactive materials present in the oil samples. Some possible mechanisms for the degradation of different oil samples and the effect of olefins on the oil samples is shown in Figure 2, 3 and 4.

CONCLUSION

Ageing work on LCO and LWGO samples doped with aliphatic olefinic isomers shows that the effects of the isomers on LCO and LWGO are not the same. The olefinic isomers seem to degrade the storage stability of LCO in the order, terminal olefins < internal olefins < branched chain olefins. Contrary to what happens in LCO, the aliphatic olefinic isomers seem to improve the storage stability of LWGO in the order, terminal olefins > internal olefins > branched chain olefins. The addition of terminal aliphatic olefins up to 9% by weight showed that the higher the percentage of the aliphatic olefins in the LWGO, the more stable the LWGO samples become. This phenomena was not caused by the dilution effect of the terminal aliphatic olefins because the addition of lower specific gravity SRD to the LWGO samples did not cause any reduction in the total insolubles. The maximum effect of any of the aliphatic olefin classes, added at a reasonable concentration of 3%, was modest, and of the order of 10% or less, if test repeatability is considered.

The observation of existent soluble gum on LWGO samples shows that internal olefins have greater effects on the existent soluble gum properties compared with that of terminal and branched chain olefins. The amount of soluble gum in the diesel doped with internal olefins, both for fresh and aged samples, is about four to six times that of the diesel doped with terminal or branched chain olefins.

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REFERENCES

1. Power, A.J. and Solly, R.K., Fuel, 1990, **69**, 292-1297.

2. Cookson, D.J., Latten, J.L., Shaw, I.M. and Smith, B.E., Fuel, 1985, **64**, 509-519.

3. Halsall, R., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 722-737.

4. Smith, R.J. and Palmer, L.D., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 875-886.

5. Taylor, W.F. and Frankenfeld, J.W., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 496-511.

6. Schrepfer, M.W., Arnold, R.J. and Stansky, C.A., Oil and Gas Journal, 1984, 79-84.

7. White, E.W., ASTM, STP, 531, 143-166.

8. Palmer, L.D. and Copson, B.V., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 902-914.

9. Fookes, C.J.R. and Walters, C.K., Fuel, 1990, **69**, 1105-1108.

10. Jones, L. and Li, N.C., Fuel, 1983, **62**, 1156-1160.

11. Bahn, O.K., Brinkman, D.W., Green, J.B and Carley, B., Fuel, 1987, **66**, 1200-1214.

12. Beranek, L.A., Baran, I.J., McVea, G. and Solly, R.K., Report MRL-R-986, Materials research laboratories, Melbourne, 1986.

13. Batts, B.D. and Fathoni, A.Z., Energy and fuels, 1991, **5**, 2-21.

14. Hazzlet, R.N., Power, A.J., Kelso, A.G and Solly, R.K., Report MRL-R-986, Materials research laboratories, Melbourne, 1986.

15. Sauer, R.W., Weed, A.F. and Headington, C.E., A Prepr. Div. petr. chem. of Am. chem. soc. **3**, 95-113, 1958.

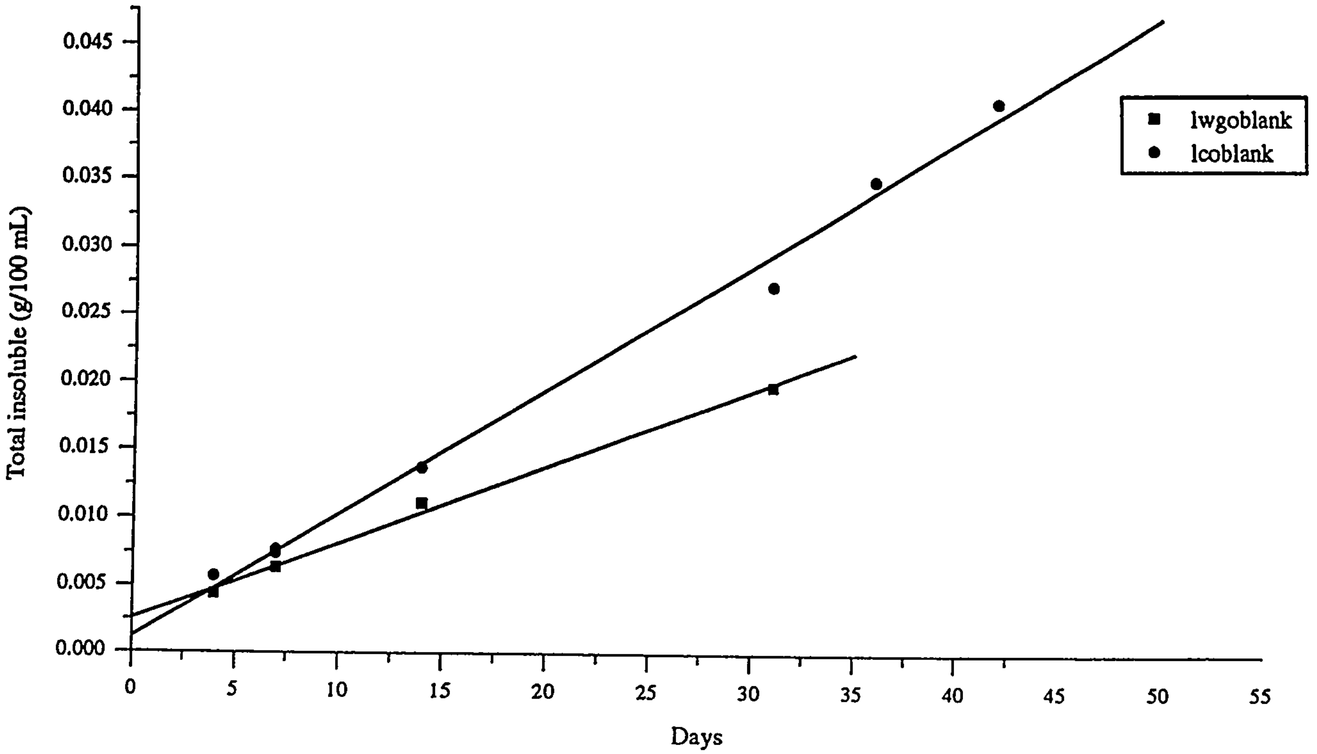
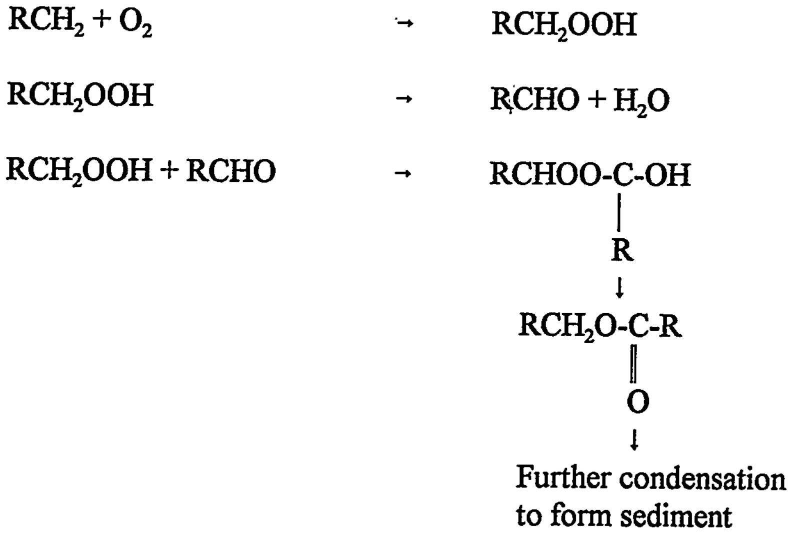


Figure 1: Total insolubles versus period of ageing



$RCH_2 + O_2 \rightarrow RCH_2OOH$

$RCH_2OOH \rightarrow RCHO + H_2O$

$RCH_2OOH + RCHO \rightarrow RCHOO\text{-}\underset{\underset{R}{|}}{C}\text{-}OH \downarrow RCH_2O\text{-}\underset{\underset{O}{\|}}{C}\text{-}R$

$\downarrow$

Further condensation
to form sediment

Figure 2: Degradation mechanism in LCO blank and olefins doped LCO

$$
\begin{array}{lcl}
RH + O_2 & \rightarrow & R^{\bullet} + HO_2 \\
R^{\bullet} + O_2 & \rightarrow & RO_2^{\bullet} \\
RO_2^{\bullet} + RH & \rightarrow & ROOH + R^{\bullet} \\
 & & \quad\downarrow \\
 & & RO^{\bullet} + HO^{\bullet} \\
 & & \quad\downarrow RH \\
 & & ROH + HOH + R^{\bullet} \\
 & & \quad\downarrow \\
 & & \text{Further reaction to form sediment}
\end{array}
$$

Figure 3: Degradation mechanism in LWGO blank

$$
\begin{array}{lllcl}
RH & + & O_2 & \rightarrow & R + HO_2^{\bullet} \\
R^{\bullet} & + & O_2 & \rightarrow & RO_2^{\bullet}
\end{array}
$$

$$
\left.
\begin{array}{lllcl}
RO_2 & + & C=C & \rightarrow & ROOC\text{-}C^{\bullet} \\
 & \textit{and/or} & & & \\
R^{\bullet} & + & C=C & \rightarrow & RC\text{-}C^{\bullet}
\end{array}
\right\}
\quad \text{Further reaction to form soluble gum, or act as inhibitor}
$$

Figure 4: Degradation mechanism in olefin doped LWGO

Table 1: Effect of ageing periods on the total insolubles (100 mL, O_2 presaturated, 80° C)

Day	Total Insolubles (g/100 mL)				
	SRD	ADO	HTD	LCO	LWGO
4	0.0000	-	-	0.0057	0.0044
7	0.0000	0.0004	0.0004	0.0075	0.0064
10	-	0.0005	0.0006	-	-
14	0.0002	0.0006	0.0012	0.0137	0.0111

Table 2: The effect of olefin doping on LCO (100 mL, O_2 presaturated, 80° C, 31 days)

Code	Dopant	Properties		
		Insoluble	Adherence	Total Insoluble
		g/100 mL	g/100 mL	g/100 mL
44-LCO	-	0.0132	0.0141	0.0273
45-LCO	3% C.ter.	0.0044	0.0259	0.0303
46-LCO	3% C.int.	0.0045	0.0266	0.0311
47-LCO	3% C.br.	0.0039	0.0285	0.0324

C.ter = Terminal olefin

C.int. = Internal olefin

C.br. = Branched chain olefin

Table 3: Aged SRD doped with terminal olefin (100 mL, O_2 presaturated, 80° C, 7 days)

Code	Conc. wt%	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/100 mL	g/50 mL
1-SRD	0	0.0000	0.0000	0.0000	0.0005
10-SRD	3	0.0001	0.0001	0.0002	0.0012
11-SRD	6	0.0001	0.0001	0.0002	0.0008
40-LWGO	0	0.0040	0.0024	0.0064	0.0289
36-LWGO	3	0.0045	0.0012	0.0057	0.0280
37-LWGO	6	0.0034	0.0017	0.0051	0.0235
34-LWGO*	0	0.0028	0.0083	0.0111	0.0405
39-LWGO*	3	0.0023	0.0063	0.0086	0.0290

Conc. = Concentration of the dopant, * Ageing extended to 14 days

Table 4: Aged LWGO doped with olefins (100 mL, O_2 presaturated, 80° C, 7 days)

Code	Dopant	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/10 mL	g/50 mL
40-LWGO	-	0.0040	0.0024	0.0064	0.0289
36-LWGO	3% C.ter.	0.0045	0.0012	0.0057	0.0280
35-LWGO	3% C.int.	0.0044	0.0018	0.0062	0.1047

Table 5: Aged LWGO doped with olefins (100 mL, O_2 presaturated, 80° C, 14 days)

Code	Dopant	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/100 mL	g/50 mL
34-LWGO	-	0.0028	0.0083	0.0111	0.0405
39-LWGO	3% C.ter.	0.0023	0.0063	0.0086	0.0290
38-LWGO	3% C.int.	0.0024	0.0081	0.0105	0.0897

Table 6: Aged LWGO doped with C_{16} olefin (100 mL, O_2 presaturated, 80° C, 7 days)

Code	Dopant (C_{16})	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/100 mL	g/50 mL
40-LWGO	-	0.0040	0.0024	0.0064	0.0289
41-LWGO	3% C.ter.	0.0036	0.0012	0.0048	0.0251
42-LWGO	3% C.int.	0.0032	0.0020	0.0052	0.1500
43-LWGO	3% C.br.	0.0023	0.0042	0.0065	0.0253

Table 7: LCO doped with olefins (50 mL, 80° C, 31 days)

No.	Total Insolubles in aged LCO (g/50 mL)			
	Blank	Doped with 3 wt% olefins		
		Terminal	Internal	Branched
1	0.0130	0.0131	0.0150	0.0150
2	0.0133	0.0133	0.0144	0.0147
3	0.0127	0.0139	0.0138	0.0156
Mean	0.0130	0.0134	0.0144	0.0151
Std. Deviation	0.0003	0.0004	0.0006	0.0005

Table 8: LWGO doped with olefins (50 mL, 80° C, 31 days)

No.	Total Insolubles in aged LWGO (g/50 mL)			
	Blank	Doped with 3 wt% olefins		
		Terminal	Internal	Branched
1	0.0088	0.0073	0.0081	0.0085
2	0.0084	0.0068	0.0081	0.0081
3	0.0089	0.0076	0.0078	0.0085
Mean	0.0087	0.0072	0.0080	0.0084
Std. Deviation	0.0003	0.0004	0.0002	0.0003

Table 9: Addition of terminal olefins to LWGO (50 mL, 80° C, 31 days)

No.	Total Insolubles in aged LWGO (g/50 mL)				
	0%	1.5%	3%	6%	9%
1	0.0088	0.0079	0.0073	0.0073	0.0059
2	0.0084	0.0087	0.0068	0.0073	0.0065
3	0.0089	0.0090	0.0076	0.0060	0.0055
Mean	0.0087	0.0085	0.0072	0.0069	0.0060
Std. Dev^n	0.0003	0.0006	0.0004	0.0007	0.0005

Table 10: Soluble existent gum of LWGO samples

Dopant	Existent soluble gum of LWGO						
	Aged (80° C)				Fresh		
	C_{16} (7 days)		C mix (14 days)		C_{16}	C mix	
	g/5 mL	g/50 mL	g/5 mL	g/50 mL	g/5 mL	g/5 mL	g/50 mL
Blank	0.0025	0.0289	0.0033	0.0405	-	0.0002	0.0026
3% ter.	0.0014	0.0251	0.0026	0.0290	0.0004	-	-
3% int.	0.0119	0.1500	0.0066	0.0897	0.0319	0.0146	-
3% br.	0.0021	0.0253	-	-	-	-	-

C mix = mixture of olefins with carbon atom number C_{12}, C_{14}, C_{16}, C_{18} and C_{20}

ter. = terminal olefins
int. = internal olefins
br. = branched chain olefins

Table 11: The effect of SRD to the stability of LCO and LWGO(50 mL, 80° C, 31 days)

Code	SRD wt%	Properties		
		Insoluble	Adherence	Total Insoluble
		g/50 mL	g/50 mL	g/50 mL
132-LCO	0	0.0024	0.0108	0.0132
140-LCO	3	0.0024	0.0110	0.0134
124-LWGO	0	0.0012	0.0078	0.0090
127-LWGO	3	0.0014	0.0090	0.0104
130-LWGO	6	0.0011	0.0088	0.0099

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CHEMISTRY OF SEDIMENT FORMATION AND ADDITIVE RESPONSE IN CRACKED MIDDLE DISTILLATES

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ABSTRACT

The current trend in middle distillate maximization is to blend significant proportions of cracked stocks.This blending enhances instability of the product which creates application problems.In order to reduce/prevent sediment formation it is essential to understand the chemistry of sediment formation. Further knowledge of sediment precursors in cracked middle distillates facilitates in screening of the suitable additives and in studying their response in prevention of sediment formation.The present paper discusses the characterization of sediment precursors, separated through methanol extraction,employing derivatization technique and FTIR spectroscopy.The effct of few commercial additives on the stability of cracked fuels both under accelerated conditions and ambient storage have also been studied. The study indicated that performance of an additive in cracked middle distillate fuels depends on fuel composition,additive structure and fuel storage conditions. From the comparision of FTIR spectra,it has been concluded that methanol extracts the sediment precursors.

INTRODUCTION

In recent era one of the problem encountered in the petroleum Industry is the instability of middle distillate fuels. With the increasing demand of middle distillates,these secondary processed products such as light cycle oil, total cycle oil, visbroken middle distillates, coker distillates etc are blended with straight run to maximize the diesel oil yield.These cracked products right from the starting when they are produced through secondary processes start degradating to produce sediments and adherent gum which ultimately cause plugging of the fuel filters and blockage of engine components[1-2].Stabilization of the cracked stocks, can be achieved by doping with additives hydrotreatment, caustic scrubbing, acid or fuel stability foam (FSF) treatment[2].

The components mainly responsible for deterioration of cracked products are mono-olefines, diolefines, nitrogen and sulfur containing polar compounds,di and polynuclear aromatics. Even on hydrogenation, it is difficult to stabilize the cocker distillates because most of the polynuclear aromatics converts into mono and di-nuclear aromatics. These types of compounds produced peroxy radicals on oxidation where as olefines polymerizes to form gum and sediments. Some esterification type reaction are also involved in degradation of these fuels.The chemistry behind degradation is very complicated and still needs lot of work to understand[1-5].

In the present paper a study has been done on light cycle oil derived from FCC unit of an Indian refinery to improve the stability employing additive doping and methanol extraction.The methanol extracted residue was characterized for the functional groups by derivatization technique and FTIR.

EXPERIMENTAL

Samples: The fuel samples used in the present study consisted of light cycle oil(sample A) and blend of light cycle and heavy naphtha in ratio of 2.6:1 (sample B).Samples C,D,E & F were obtained by blending straight run distillate with sample B in 50:50, 60:40, 70:30, and 80:20 ratio respectively. All samples were characterized for their physico-chemical and distillation characteristics which are given in Table-1 & Fig 1,respectively.

STABILITY DETERMINATION

Stability of the above samples were determined using following methods.

The UOP 835-82 blotter test and modified ASTM D-2274 have been employed to study the accelerated stability of various fuels[6].

The modified ASTM D-4625 test method have been used to measure the long term storage stability.

EFFECT OF ADDITIVES ON THE STABILITY OF THE FUEL SAMPLES.

Light cycle oil and its blend with heavy naphtha were doped with three commercial additives (400ppm and 800ppm concentration) separately and stability of the doped samples were determined as in case of the original fuel samples. Results are given in Table-2.

EXTRACTION WITH METHANOL.

For extraction, fuel sample and methanol in the ratio 5:2 were shaken in a separating funnel for 10 minutes.The mixture was then centrifuged at 2000 rev min^{-1} for 10 minutes.The upper methanol phase and lower fuel phase were separated.The yield of extracted fuel (lower layer) was 94-97%. Together with the sediment precursors, a small quantity of the fuel also went into the methanol layer. The yield of the methanol residue obtained after evaporation of the methanol was 0.05-0.07 wt%. The extracted fuel was then examined for stability as for the original sample.

CHARACTERIZATION OF SEDIMENT PRECURSORS.

The light cycle oil (without removing gum precursors) was also stored under ambient conditions for 26 months and the total gum formed was separated quantitatively. After removing the total gum formed on 26 months ambient storage,the remaining distillate fuel has been extracted with methanol for isolating the remaining gum precursors. These precursors were acetylated, benzoylated & hydrolysed separately[7] in order to assign different types of molecular moieties responsible for gum formation. All the methanol extracts were studied empolying FTIR spectrometer for qualitative assignment / characterization of functional groups. Spectra were recorded by preparing thin films of the samples depositing from the dichloromethane solution on KBr windows using

PE 1760 X FTIR instrument.

RESULTS AND DISCUSSION

The physico-chemical characteristics of various blended fuels show an increasing trend in almost all the physical properties as the percentage of straight run is increased in them (Table-1 and Fig.2).

Stability data of these fuel samples before and after treatment with different additives have been reported in Table-2. The response of additives depends mainly on the interaction of additives with the chemical constitution of fuel, the type of storage vessel and external conditions like temperature, availability of oxygen, static or dynamic conditions.Results shown in Table-1 indicate that total insolubles formation in different stability methods are much higher in light cycle oil (sample A) compared to the blend of light cycle oil and heavy naphtha (sample B), which reveals that light cycle oil is mainly controlling the tendency of the fuel towards instability. The percentage reduction data of doped samples in Table-2 further indicate that all the three additives used in the present study are effective in reducing the total insolubles formation in both the fuel samples as measured by modified ASTM D-2274 and ASTM D-4625 methods.

The reduction in sediment formation after doping the fuel with additives under ASTM D-4625 test method depicts that the effectiveness of all the additives in LCO reduces with time.This behaviour has already been explained due to participation of additives in sludge formation with increase in time[8]. It is also evident that % reduction of insolubles in accelerated test under dynamic conditions of modified ASTM D-2274 in the presence of oxygen is more pronounced after doping with additives due to better additive fuel interaction under these conditions. But in case of static conditions (ASTM D-4625) as the oxygen availability is limited and agitation is also not there, the overall % reduction after doping with additives are comparatively less.

Figs.2,3 and Table-3 indicates the effect of methanol extraction on the stability of fuel samples A to F. From the results given in Table-3 it is evident that the initial pad rating of light cycle oil is 15 which is reduced to 6 by methanol extraction. Generally a pad rating of 7 is considered satisfactory for shipment[10]. Significant lowering of pad rating is observed in all samples A to F after extraction. Improvement in the colour before and after aging has also been observed in all the fuel samples through methanol. Fig.2,reveals the effect of methanol extraction on the sediment of fuel samples measured under accelerated conditions by modified ASTM D-2274. The percentage reduction of sediments in light cycle oil (sample A) is 31.8 where as in blend (sample B) it is only 22.7.It also reveals that percentage reduction in sediments is increasing as the ratio of straight run is increasing in blends samples C to F. The percentage reduction of adherent gum afer methanol extraction is much higher than sediments in samples A and B (Fig.3). The same trend is observed in % reduction of sediments in blends (samples C to F). Since methanol extraction has a great influence on the stability in light cycle oil compared to other samples, it is clear that the chemical precursors responsible for the instability of middle distillate fuels are predominantly present in light cycle oil (sample A) and are soluble in methanol.

Stability of these samples (A to F) after storing for three months at 43.3°C reveals that adherent gum is reduced by 53.3% in sample A and 42.2% in sample B and the % reduction is increasing on increasing the ratio of straight run.In non vented conditions, % reduction of adherent gum is higher compared to vented conditions in samples A and B (Table-4). Sample A after removing the sediments (18.6 mg/100ml) and adherent gum (1.2 mg/100ml) formed during ambient storage of 26 months was extracted with methanol alone and in presence of 4N sodium carbonate / sodium acetate solution (100ml sample 40 ml methanol and 0.2 ml 4N sodium carbonate and 4N sodium acetate solution) to study the effect of pH / medium on the effectiveness of methanol extraction.This shows greater reduction of sediments in presence of sodium acetate compared to methanol as such and with 0.2 ml of 4N sodium carbonate solution. But presence of sodium acetate incresed the adherent gum as compared to other two mediums. Thus the total insolubles in sodium acetate medium has increased. This is perhaps due to the participation of acetate ion in the formation of esters during insolubles[8].

The comparison of spectra of acetylated recovered residue (Fig.5) with methanol extract (Fig.4) depicts the decrease in -OH, -NH peak intensity as obtained from absorbance ratio of this peak with C-H streching peak (2923cm^{-1}). This is reduced from 0.686 to 0.175. The presence of a carbonyl peak at 1732cm^{-1} in the acetylated product indicates the formation of ester. This confirms the presence of phenols and alcohols in the methanol extracts. However the amines present in the exract may also be acetylated to form acetanilides yielding carbonyl bands at 1761 and 1713cm^{-1} in the product adhered with the wall of the reaction flask (spectra not given). This has further been confirmed by the presence of bands in the region 1000-1250cm^{-1} due to aliphatic C-N groups.This supports the drastic reduction in the OH/NH bands of aryl/alkyl -OH and amine type -NH groups.

The examination of the FTIR spectra of benzoylated product of methanol extract (Fig.6) reveals the presence of strong carbonyl peak at 1685cm^{-1} due to $Ar-\overset{\overset{O}{\|}}{C}-N<$ structures. A medium intensity peak at 1785cm^{-1} may be due to ester of $-\overset{\overset{O}{\|}}{C}-O-Ar$ type. The presence of a small band at 1587cm^{-1} due to N-H bending also supports the benzoylation of amines. The bands in the region 1000-1300cm^{-1} also confirms these assignments .The disappearance of band in the OH/NH region of benzoylated product reveals that almost all the functional group like alcoholic & phenolic -OH, pyrollic & amine and amidic type -NH, have taken part in the reaction.This further confirms the presence of alcoholic and phenolic -OH,pyrrolic, amine and amidic -NH groups in the methanol extract.

In order to further confirm the presence of -OH and -NH containing molecules, hydrolysis of the methanol extract was done with 20% NaOH. The spectra of unhydrolysed part (Fig.7) shows the presence of sharp bands at 3472,3412 and 1595cm^{-1} due to pyrollic and amine type -NH streching and bending vibrations respectively, while the spectrum of hydrolysed part (Fig.8) shows the presence of -OH band at 3463cm^{-1} which shifts to 3334cm^{-1} on concentrating the sample due to H-bonding.The bands at 1654 and 1709cm^{-1} show the presence of amidic carboxyl groups. Thus the comparison of the bands in Figs.7 and 8 reveals that amine and pyrollic structures are not hydrolysed while phenolic/alcoholic and amidic structures have gone with the hydrolysed material.This further confirms the presence of aryl & aliphatic -OH, pyrollic, amine and amidic -NH, and carbonyl in the methanol extract. Derivatization of different functional groups of methanol extracts depicts that the nature of -OH group is aryl/alkyl hydroxyl type, -NH group is amine, and/or pyrollic type while carbonyl group is of amidic and/or carboxylic type.Similar functional groups have been found to occur in the sediments of these fuels[7].

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REFERENCES

1. Taylor,W.F; & Frankenfeld,J.W. In proceedings of the 2nd International Conference on Long term Storage Stability of Liquid Fuels.(Eds. L.L.Stavinoha) Institute of Petroleum, London.1986 p 496.
2. Batts ,B.D; & Fathoni, A.Z; Energy Fuels. 1991,5,2
3. Dorbon,M & Bernasconi,C. Fuel 1989,68,1067.
4. Sutterfiel,W.V; Steele,D.G; Archer,D.G; etal.In proceedings of the 3rd International Conference on Long term Storage Stability of Liquid Fuels.(Eds.R.W.Hiley; R.E.Penfold; J.F.Pedley). Institute of Petroleum,London 1988,p 472.
5. Hardy D.R; & Wetcher, M.A. Energy Fuels. 1990,4,270
6. Sharma, Y.K; & Agrawal,K.M. Fuel.1994, 73,269
7. Power, A.J; & Mathys,G.I. Fuel. 1992, 71,903
8. Sharma, Y.K.;Singh,I.D; Aswal,D.S; & Agrawal, K.M. ACS symposium Div.of Fuel Chemistry , Washington DC, Aug 21-24 1994.
9. Bowman, D.F; Middleton,B.S; & Ingold,H.U. J. Org. Chem. 1969,34 3456.
10. Mabley, P.B; & Wallace,G.M; In proceedings of the 3rd International Conference on Long term Storage Stability of Liquid Fuels (Eds.R.W.Hiley;R.E.Penfold J.F.Pedley), Institute of Petroleum,London 1988,p 412.

FIG.1 DISTILLATION CHARACTERISTICS OF THE FUEL SAMPLES (ASTM D-2887)

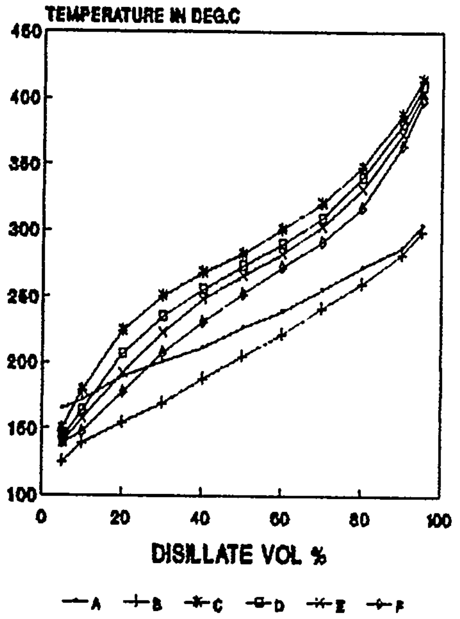


FIG.2 EXTRACTION EFFECT ON THE STABILITY IN TERMS OF THE SEDIMENTS IN DISTILLATE FUEL (METHOD MODIFIED ASTM D-2274)

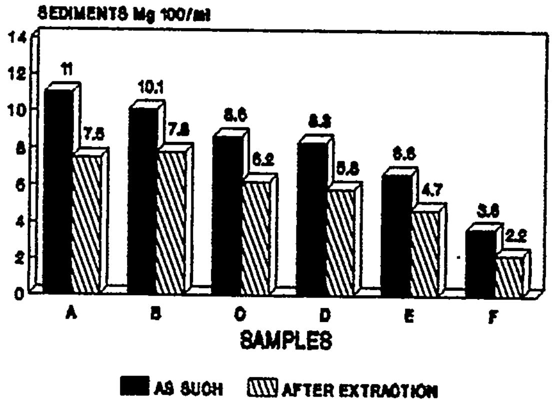
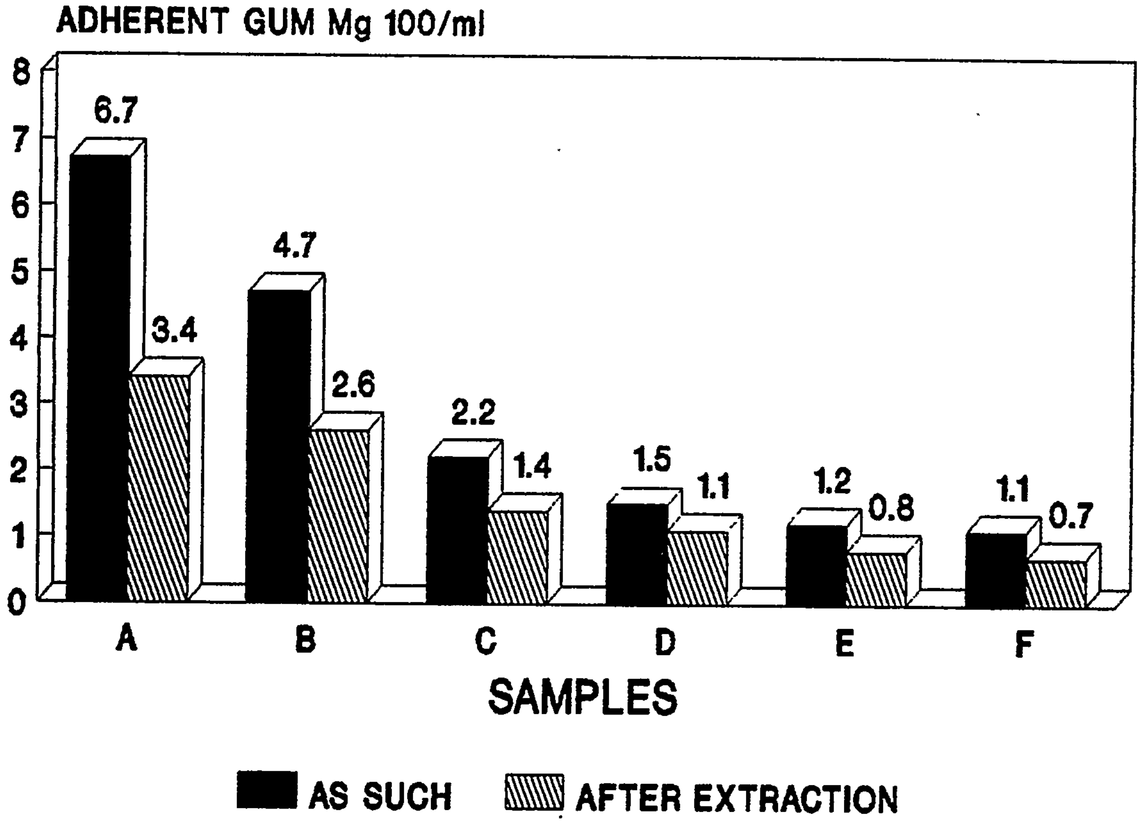


FIG.3 EXTRACTION EFFECT ON THE STABILITY IN TERMS OF ADHERENT GUM IN DISTILLATE FUEL (METHOD MODIFIED ASTM D-2274)



FTIR SPECTRA OF DERIVATIZED PRODUCTS

FIG 4 : METHANOL EXTRACT RESIDUE

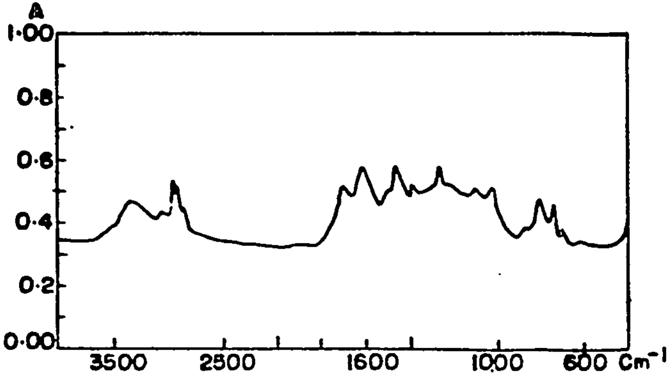


FIG 5 : RECOVERED ACETYLATE RESIDUE

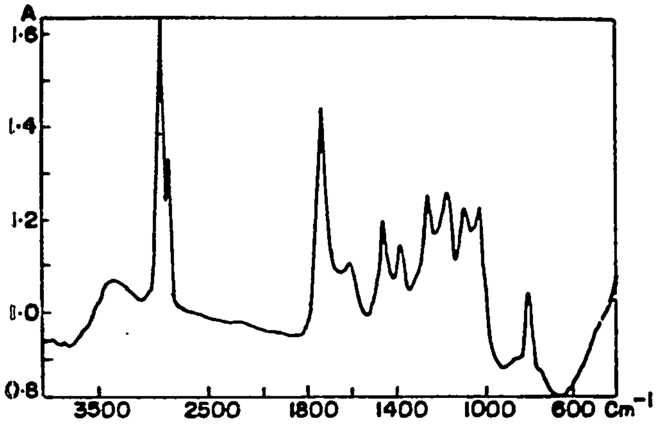


FIG 6 : BENZOYLATED RESIDUE

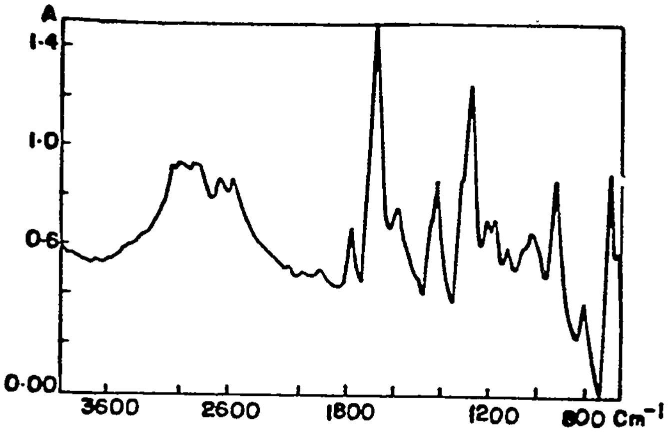


FIG 7 : UNHYDROLYSED RESIDUE

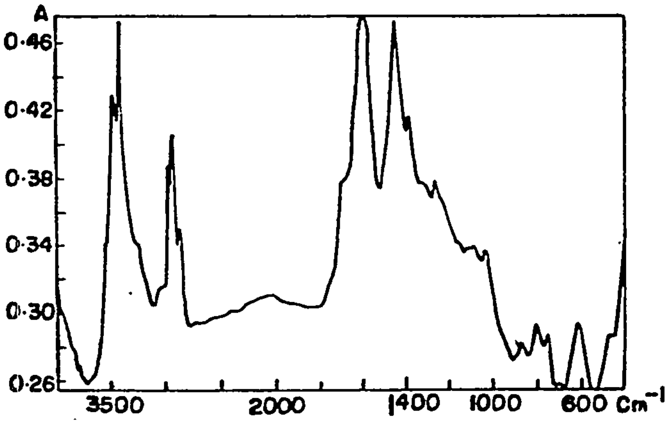


FIG 8 : HYDROLYSED RESIDUE

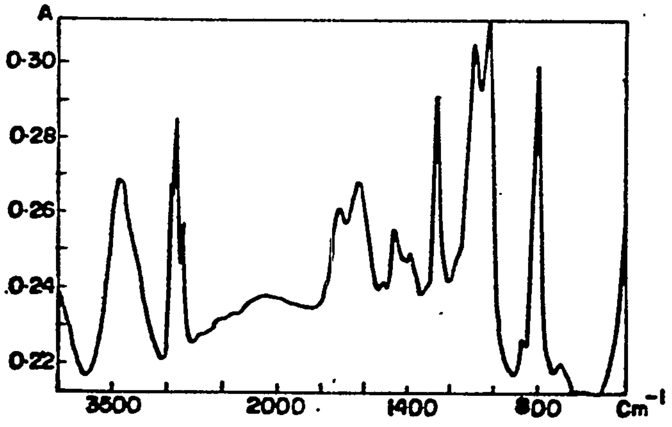


TABLE-1

Physical Properties Of The Fuel Samples

	CHARACTERISTICS					
	A	B	C	D	E	F
Density at 20°C	0.8542	0.8307	0.8368	0.8380	0.8389	0.8401
Kinematic Vis.at 40°C in cSt.		1.16	1.68	1.92	2.12	2.43
Acidity mg KOH/gm	0.0756	0.0546	0.0335	0.0421	0.0489	0.0538
Sulphur%Wt	0.3046	0.183	0.1684	0.1713	0.1738	0.1770
Aniline Point °C	31.0	33.0	58.8	63.2	66.8	71.2
Colour ASTM	5.5	5.0	<4.0	3.5	3.0	2.5
Molecular Weight	196	210	179	195	200	207
Nature	Light Cycle Oil	Light Cycle Oil+Heavy-naphtha	-----Light Cycle Oil,Heavy Naphtha & Straight Run Blends------			

TABLE-2

RESPONSE OF ADDITIVES ON STABILITY OF MIDDLE DISTILLATE FUEL SAMPLES *

	Sample A (Light cycle oil)				Sample B (LCO + Heavy Naphtha)			
	As such	with Additive	with Additive	with Additive	As Such	with Additive	with Additive	with Additive
		A1	A2	A3		A1	A2	A3
Colour ASTM	5.5	5.5	5.5	6.0	5.0	5.0	5.0	5.5
% Transmittance	59.73	55.72	55.45	53.75	67.6	67.48	74.69	60.57
After accelerated aging								
Colour ASTM	<7.0	6.0	6.5	7.5	6.0	<5.5	5.5	6.5
% Transmittance	45.59	61.48	45.75	38.78	60.22	73.31	67.88	48.06
% Reduction of total insolubles								
ASTM D-2274	(17.7)**	66.7	55.9	38.4	(14.8)**	32.4	4.05	11.5
ASTM D-4625								
One week at 43.3°C	(8.0)**	47.5	65	55	(7.0)**	17.1	28.6	20
Three weeks at 43.3°C	(8.2)**	29.3	63.4	48.8	(7.4)**	16.2	27.0	21.6
Twelve weeks at 43.3°C	(9.4)**	31.9	42.6	34.0	(9.0)**	13.3	15.6	33.3

---

* Additives Concentration A1 & A2 (400ppm), A3 (800 ppm).

** Total insolubles,mg/100ml

TABLE 3

EFFECT OF METHANOL EXTRACTION ON THE STABILITY OF FUEL SAMPLES.

(STABILITY DETERMINED BY METHOD UOP 835-82)

SAMPLE	A		B		C		D		E		F	
	1	2	1	2	1	2	1	2	1	2	1	2
Pad Rating	15	6	14	6	13	6	9	6	8	5	7	4
BEFORE AGING												
ASTM Colour	5.5	<5	5	<4.5	<4	<3.5	<3.5	3	3	2.5	2.5	2
Absorbance at 650 nm	0.224	0.168	0.170	0.145	0.163	0.129	0.156	0.109	0.134	0.094	0.123	0.083
AFTER AGING												
ASTM Colour	<7	5	6	5	4.5	<3.5	<4.5	<3.5	<4.0	<3	3	2.5
Absorbance at 650 nm	0.364	0.181	0.220	0.193	0.216	0.112	0.207	0.109	0.189	0.088	0.065	0.037

1 Original

2 After Extraction

TABLE 4

EFFECT OF METHANOL EXTRACTION ON THE LONG TERM STORAGE STABILITY OF FUEL SAMPLES

(STABILITY DETERMINED BY MODIFIED ASTM D-4625 STORAGE FOR THREE MONTHS AT 43.3°C)

SAMPLES	A		B		C		D		E		F	
	1	2	1	2	1	2	1	2	1	2	1	2
NON VENTED												
Adherent Gum mg/100ml	6.0	2.8	4.5	2.6	4.2	3.0	4.2	2.8	3.0	1.8	2.4	0.8
Total Insoluble, mg/100ml	9.471	6.6	9.0	7.6	8.4	7.4	8.2	7.0	6.4	5.0	4.6	3.0
VENTED												
Adherent Gum mg/100ml	6.2	4.6	5.4	3.8	4.2	3.0	4.2	4.0	3.2	1.8	2.4	0.8
Total Insoluble, mg/100ml	9.8	5.0	9.2	7.8	8.6	7.6	8.4	7.2	6.4	5.2	4.8	3.0

1 Original 2 Afer Extraction

TABLE 5

EFFECT OF METHANOL EXTRACTION ON THE STABILITY UNDER DIFFERENT MEDIUM CONDITIONS (STABILITY DETERMINED BY MODIFIED ASTM D-2274)

SAMPLES	LCO*	LCO extrated by CH_3OH**	LCO extrated by CH_3OH** 0.2ml of 4N Na_2CO_3	LCO extracted by CH_3OH** 0.2 ml of 4N CH_3COONa
BEFORE AGING				
Transmittance % at 650 nm	46.67	60.72	58.75	61.56
ASTM Colour	<6.5	<6.0	5.0	<5.5
AFTER AGING				
Transmittance % at 650 nm	-	52.08	61.71	70.80
ASTM Colour	<6.5	6.0	<5.5	<5.0
Sediments mg/100ml	14.0	10.5	9.7	8.2
Adherent Gum mg/100ml	3.2	0.7	o.7	2.8
Total Insoluble,mg/100ml	17.2	11.2	10.4	11.0

* LCO obtained after 26 months ambient storage and removing the insolubles.
** Fuel methanol ratio 5:2

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A STUDY OF THE SAFETY OF THE ASTM D5304 OXYGEN OVERPRESSURE STABILITY TEST

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ABSTRACT

While the test method for assessing distillate fuel storage stability by oxygen overpressure was being evaluated as a potential ASTM standard, a question of its safety was raised, specifically whether the juxtaposition of liquid fuel and oxygen at elevated pressure could lead to explosive self ignition. As a consequence, the authors conducted a literature search followed by a small experimental program. The results of those studies show that the temperature and pressure used in Test Method D5304 are probably safely below the conditions that would lead to autoignition of normal middle distillate fuels. However, middle distillate fuels of unknown or unusual sources, or containing additives, e.g. ignition improvers, should be screened before evaluating their stability by Test Method D5304.

INTRODUCTION

In the mid 1980's, research scientists and engineers at the Naval Research Laboratory (NRL) and at the Carderock Division (CARDEROCKDIV) of the Naval Surface Warfare Center began to explore the possibility of developing an accelerated stability test using oxygen at elevated pressures to reduce either the test duration, the test temperature, or both. In May 1986, the two laboratories began a joint study of the times, temperatures, and oxygen pressures used during the stress period of the test; and by early 1987, the two laboratories agreed to draft a standard procedure using an NRL low pressure reactor and to conduct mini round robin interlaboratory tests. Hardy et al[1] presented results of some early work at the 3rd International Conference, in London in September 1988.

The procedure was eventually standardized as ASTM Test Method D5304-92 for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure. The test method is considered applicable to ASTM Specification D975 Grades 1D and 2D diesel fuels, to NATO F-76 fuels such as U.S. Military Specification MIL-F-16884H Naval Distillate Fuel, and similar middle distillate fuels.

In the test, a 100 mL aliquot of filtered fuel is placed in a borosilicate glass container which is then put into a pressure vessel. The vessel is pressurized with oxygen to 800 kPa absolute (115 psia) and placed in a forced-air oven controlled at 90°C, where it remains for 16 hours. The pressure vessel and its contents are cooled to ambient temperature (roughly 25°C) before the insoluble products formed during the stress period are determined gravimetrically.

Like other fuel storage stability tests, the results are not indicative of the amount of sediment that might be produced in a given storage situation because storage tank construction and ambient conditions are too variable. The results are, however, considered representative of the inherent stability of a fuel and are useful in ranking fuels.

In response to one of the numerous ballots to which ASTM standards are subjected, a voter challenged the safety of the procedure on the premise that self-ignition could occur when hydrocarbon fuels and oxygen are in contact at elevated temperatures and pressures. CARDEROCKDIV was asked to explore the that concern.

TERMINOLOGY

There are a number of synonyms or related terms for self-ignition temperature (SIT). The most common, and the one used in this paper, is the autoignition temperature (AIT). Occasionally, the term autogenous ignition temperature is used. The term spontaneous ignition temperature has also been used but suffers from possible confusion with the spontaneous combustion of paint rags and similar phenomena. Definitions of some pertinent terms are provided below to clarify the AIT concept:

> **autoignition** - the ignition of a material, commonly in air, as the result of heat liberation due to an exothermic oxidation reaction in the absence of an external ignition source such as a spark or flame.[2]
>
> **autoignition temperature** - the minimum temperature at which autoignition occurs under the specific test conditions.
>
> **flash point** - the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg) at which application of a test flame causes the vapor of a specimen to ignite under specified conditions of test.[3]

The definition of flash point is included to show its close correspondence, except for the presence of a test flame, to AIT.

APPROACH

Our original plan was first, to ascertain what was known of the self-ignition of fuels through an examination of the technical literature and, second, to conduct laboratory experiments to provide missing information. There were four objectives of the literature search:

- To determine what mechanisms had been postulated for fuel ignition in the absence of an ignition source;

- To ascertain a reasonable range of temperatures for the autoignition of distillate diesel fuel in air at atmospheric pressure;

- To determine the effect of oxygen pressure on the autoignition temperature of distillate diesel fuels;

- To ascertain whether there are standardized tests for measuring the self-ignition temperatures under elevated oxygen pressures.

CARDEROCKDIV, using handbooks and technical literature on combustion, addressed the first three objectives. ARTECH CORP. was contracted to address the fourth objective and to conduct a computer search of pertinent data bases.

ARTECH CORP. used the Dialog System^{R} which permits using the same commands to search a large number of commercial data base files. The following were the major files searched:

NTIS
Compendex Plus
SciSearch
World Translations Index

Kirk-Othmer Encyclopedia of Chemical Technology
Merck Index Online
Analytical Abstracts Online

Chemical Engineering Abstracts
Chemical Safety Newsbase
World Patents Index
CA Search

The smallest time frame covered by any of these data bases was five years (World Translations Index 1984 - 1989). The maximum time frame exceeded twenty years. The NTIS data base covered 1964 - 1989; the World Patents Index covered the period from 1963; and the CA Search data base covered the period 1967 - 1990.

The initial search terms were "autoignition" and "oxygen." These failed to turn up any pertinent literature, so the search was broadened to include such terms as "ignition" and "flash point" in addition to "oxygen."

LITERATURE SEARCH RESULTS

Mechanisms of Autoignition - Jost[4] identified two processes by which explosions of a combustible gas mixture can occur. One is the process of thermal explosion; the other is the process of branched chain explosions. Autoignition is considered to be a thermal explosion type, so autoignition temperature is the lowest temperature to which a combustible mixture must be raised so that heat generated by the exothermic oxidation reaction overbalances the rate of heat loss to the surroundings.

Jost, building on the work of his predecessors, assumed that the oxidation of combustible gas is exothermic and that part of the heat is lost through the vessel walls while part goes to heat the gaseous mixture. He further assumed that the rate of oxidation, hence the rate of heat release, is an exponential function of the temperature, whereas the loss of heat through the vessel walls is a linear function of the temperature. When the heat can no longer be discharged through the vessel walls as fast as it is generated, the temperature in the reaction vessel grows rapidly and a thermal explosion occurs.

AIT Range for Distillate Diesel Fuels - We found no AIT values for diesel fuel either under atmospheric air or under elevated pressures of oxygen. We did find AIT values under atmospheric air pressure for a number of hydrocarbons and several light petroleum fractions.[5,6,7,8] Table 1, which provides a sampling of the reported data, shows considerable differences depending upon the source.

Table 1 also reveals a general decrease in the AIT as the molecular weight of compounds in a homologous series increases. For example, methane is shown to have an AIT of 537 - 749°C whereas decane is shown to have an AIT of 210 - 260°C. Consequently, we estimate that distillate diesel fuels, which have higher average molecular weights than kerosine (AIT 229 - 293°C), will have an AIT range of 220 - 280°C.

Effect of Oxygen Pressure on AIT - Jost[4] has published an equation, based on the laws of physical chemistry, that relates AIT to the pressure of the system:

$$\ln (p/T) = (E/RT) + k \qquad 1)$$

or, in its exponential form:

$$p = T(e^{k})(e^{E/2RT}) \qquad 2)$$

In this equation, ln is the natural logarithm, p is the absolute pressure of the system in kPa, T is the AIT in degrees Kelvin, E is the activation energy of the reaction, R is the gas constant, and k is a constant unique to each reactor system.

Figure 1 shows the calculated effect of oxygen pressure on the AIT. The three curves represent assumed atmospheric AIT values of 220°, 250°, and 280°C. From this figure, it is evident that, even at almost twice the test pressure of 800 kPa (115 psia), the AIT for a fuel whose atmospheric AIT is 220°C is still about 50°C above the D5304 90°C test temperature and the AIT for a fuel whose atmospheric AIT is 280°C is about 100°C above the test temperature. If the assumptions on which the equations are based are reasonably accurate, these differences between test temperature and calculated AIT values imply that the test conditions are safely below conditions that would lead to thermal explosions.

Figure 1 also shows that the effect of a given increase in oxygen pressure on AIT decreases as the pressure increases. Increasing pressure from 448 to 1137 kPa (65 to 165 psia) decreases AIT by 14° to 19°C whereas increasing pressure from 792 to 1481 kPa (115 to 215 psia) decreases the AIT by only 9° to 11°C. This is an inherent safety feature, because increasingly large pressure increases are needed to obtain a given decrease in the AIT.

Availability of Standardized Tests - The on-line literature search revealed only two standard test methods for the determination of autoignition temperature. The one method is ASTM Test Method E659 for Autoignition Temperature of Liquid Chemicals[2]. The other method is ASTM Test Method G 72[9] Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment.

Test Method E659 is limited to the determination of a liquid chemical (including hydrocarbons) in air at atmospheric pressure in a uniformly heated vessel. Ignition is defined as the appearance of a flame accompanied by a sharp rise in temperature of the gas mixture and includes both hot flames of various colors, usually yellow, and cool flames that appear as a faint bluish glow visible only in total darkness. Consequently, the test is conducted in the dark in a borosilicate flask. The test method is limited to atmospheric pressures and hence is not suitable for tests at higher oxygen pressures.

Test Method G 72 is designed for determining autoignition temperatures of liquids or solids having ignition temperatures of 60° - 424°C (140° - 800°F) in oxygen-enriched environments containing 0.5 to 100% oxygen at pressures of 2.1 to 20.7 MPa (300 to 3000 psi). The G72 apparatus has four subsystems:

oxygen compression; valving and pressure relief; instrumentation; and heating and reaction vessel. The stainless steel reaction vessel (65 mm o.d. and almost 300 mm long) weighs 9.75 kg and is designed for a maximum working pressure of 82.7 MPa (12000 psi) at 427°C (800°F).

In Test Method G 72, a 0.2 g specimen is placed in the reaction vessel and the vessel is pressurized with an oxygen-enriched gas to the desired pressure. The heating jacket around the vessel is then activated and adjusted to heat the reaction vessel at a rate of about 5°C/min until it reaches 260°C. (Above 260°C, the heater may not be able to maintain that heating rate, so a rate of over 3°C/min is allowed.) Ignition of the sample is indicated by a rapid temperature rise of at least 20°C. If no ignition occurs before the reaction vessel temperature reaches the maximum safe operating temperature of 425°C, heating is stopped, the pressure is released, and the AIT is reported as being greater than 425°C.

<u>Laboratory Experiments</u> - As stated earlier, our plan was to conduct laboratory experiments to obtain necessary information not found in the literature search. The lack of information on AIT values, under elevated oxygen pressures, for middle distillate fuels such as 1D and 2D diesel fuels, implies the need for two types of tests.

In the first type of test, we would determine the actual AIT of representative middle distillate fuels at an 800 kPa oxygen pressure, i.e. the D5304 test pressure. The AIT values obtained would be examined to ascertain how much they exceed the 90°C test temperature.

The second type of test would be a screening test conducted at 1200 to 1600 kPa, i.e. from 50% greater up to twice the pressure specified for D5304, with the pressure vessel held at the 90°. This would determine whether any of the fuels tested have AIT values as low as 90°C at pressures somewhat in excess of the specified test pressure.

The Test Method G 72 apparatus would be suitable for both types of laboratory experiments. Upon learning that there was no G 72 apparatus available for contract, we decided to build our own apparatus for screening purposes. We would not need the high pressure apparatus used in the G 72 procedure. In particular, we would need neither the compression system nor the reaction vessel capable of the high pressures for which the G 72 unit was designed. Instead, we could use oxygen cylinder pressures reduced to our selected pressure and we could use a reaction vessel similar to the one used in Test Method D525 for the oxidation stability of gasoline. The D 525 pressure vessel is constructed of type 304 stainless steel to withstand a working pressure of 180 psi (1241 kPa) at 100°C.

Such a screening system was assembled by ARTECH CORP. and several preliminary tests were conducted. Oxygen is supplied from cylinders equipped with a pressure regulator. A pressure transducer with an integral pressure relief system is used to prevent the pressure in the reaction vessel from exceeding the preset level. Three chromel-alumel thermocouple assemblies provide temperatures of the test specimen, the gas phase in the reactor, and the outer surface of the reactor. Although heat can be provided to the reactor from a heating jacket, an oil bath, an oven, or a hot plate, the hot plate was normally used.

Electrical signals from the thermocouples and pressure transducer are converted into temperature and pressure readings, respectively, by a computer. Differential temperatures, an additional way to ascertain whether an AIT has been reached, can also be obtained by the computer software.

The test procedure consists of placing a 1-gram specimen of the liquid into a microanalytical test tube. The test tube is placed in the reactor where a bed of sand serves to simultaneously support the test tube and transmit heat to the sample. The reactor is sealed, flushed with oxygen, and pressured to up to 1200 kPa with pure oxygen. The reactor is then heated at a rate of about 2.5°C/min up to a maximum temperature of 225°C while a real-time computer display shows the three temperatures and the reactor pressure. From the display, the operator can note when autoignition occurs and can stop the test.

Tests were run on eight compounds and two diesel fuels. The compounds (with published AIT values under atmospheric air) were acetone (548°C), dodecane (204°C), dodecene (AIT not available), a hexane blend (n-hexane 260°C), isooctane (418°C), methanol (464°C), nitrobenzene (482°C), and toluene (536°C). The two diesel fuels were blends of straight run and recycle stocks used in an earlier study on fuel stability additives. Neither the pure compounds nor the diesel fuels gave any evidence of having an AIT below 165°C when under 1200 kPa oxygen pressure.

Figure 2 shows the data obtained when testing dodecene under 100 psig (800 kPa) oxygen pressure. Although we have no AIT value for dodecene, it is an olefin so we would expect it to have a lower AIT than dodecane which has an AIT of 204°C under atmospheric air pressure. However, there is no evidence in Figure 2 of autoignition having occurred and there was no evidence of autoignition in the dodecane test. ARTECH CORP. personnel report detecting a rancid smell when the reactor was opened, so we are postulating that oxidation occurred before the AIT was reached so the material in the reactor was no longer dodecene. Further investigation would be required to resolve this matter.

It is our belief that the screening apparatus, which can be assembled from equipment available in a moderately equipped petroleum laboratory, should be used to alleviate concerns regarding the safety of testing any fuel sample in the D5304 test procedure, until experience supports the probable safety of using the oxygen overpressure procedure. A fuel from a new source, a fuel from a new crude oil, or a fuel containing additives with which a laboratory is unfamiliar could be cause for such concern. It is suggested that a body of laboratory data on the AIT values for typical middle distillate fuels, both neat and containing additives, would also help alleviate concerns regarding the safety of the test.

FINDINGS AND CONCLUSIONS

1. We found no AIT values for diesel fuel in our literature search but extrapolation of published AIT values for kerosine, a lower boiling distillate, leads us to conclude that AIT values under atmospheric air pressure will generally fall in the 220° to 280°C range. This is well above the 90°C operating temperature used in ASTM Test Method D 5304.

2. Calculated AIT values obtained using an equation relating AIT values to system pressure, leads us to conclude the D5304 operating temperature of 90°C is well below the anticipated AIT value at 800 kPa of oxygen pressure.

3. Preliminary screening tests run at 800 kPa of oxygen on eight compounds and on two diesel range fuels failed to produce evidence of any autoignition up to the maximum test temperature of 225°C. Because the AIT of diesel fuel under atmospheric air pressure is bracketed by the AIT values of the compounds tested, diesel fuel should not reach autoignition under the lower temperature used in Test Method D5304.

4. Although published information indicates the operating conditions of Test Method D5304 are below the autoignition region, it is advisable to confirm these indications by laboratory determinations of AIT under pressure for a number of middle distillate fuels. We recommend that industry and government undertake the development of a body of data on the autoignition temperatures of typical representative middle distillate fuels (both neat and containing typical additives) under elevated oxygen pressures.

5. We recommend the use of the screening test described as a means of checking the safety of running the D5304 oxygen overpressure test on any fuel from a new source or crude, or containing additives with which the laboratory is not familiar.

TECHNICAL REFERENCES

(1) Hardy, D. R.; Beal, E. J.; Hazlett, R. N.; Burnett, J.C. **Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels**, London, U.K., 1988; pp. 647 - 658.

(2) Test Method E 659 "Autoignition Temperature of Liquid Chemicals," in: **Annual Book of ASTM Standards**, 1993, Vol. 05.03, American Society for Testing and Materials, Philadelphia, PA

(3) Test Method D 93 "Flash Point by Pensky-Martens Closed Tester," in: Ibid. Vol. 05.01.

(4) Jost, W., Explosions and Combustion Processes in Gases, McGraw-Hill Book Co., Inc., New York, NY, 1946; pp. 3 - 46.

(5) Dean, J. A. (Ed.), Lange's Handbook of Chemistry, McGraw-Hill Book Co., Inc., New York, NY, 1985.

(6) Nelson, W. L. Petroleum Refinery Engineering; McGraw-Hill Book Company, Inc., New York, NY, 1958, pg. 201.

(7) Considine, D. M. (Ed.), Energy Technology Handbook, McGraw-Hill Book Co., Inc., New York, NY, 1977.

(8) Hawley, G. G., The Condensed Chemical Dictionary, Van Nostrand Reinhold Company, New York, NY, 1977.

(9) Test Method G 72 "Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment," in: Annual Book of ASTM Standards, 1993, vol. 14.02, American Society for Testing and Materials, Philadelphia, PA.

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Table 1 - Published AIT Values from Several Sources (AIT's in Degrees Celsius)

Substance	Lange	Nelson	Considine	Hawley
Methane	540	537	632/749	-
Pentane	260	309	-	309
Decane	210	> 260	-	250
Cetane	-	-	205	
Benzene	560	580	-	562
Ortho xylene	465	496	-	464
Cumene	425		-	424
Petroleum ether	550	246	-	-
Gasoline	280	257	260/427	
Kerosine	-	254	254/293	229

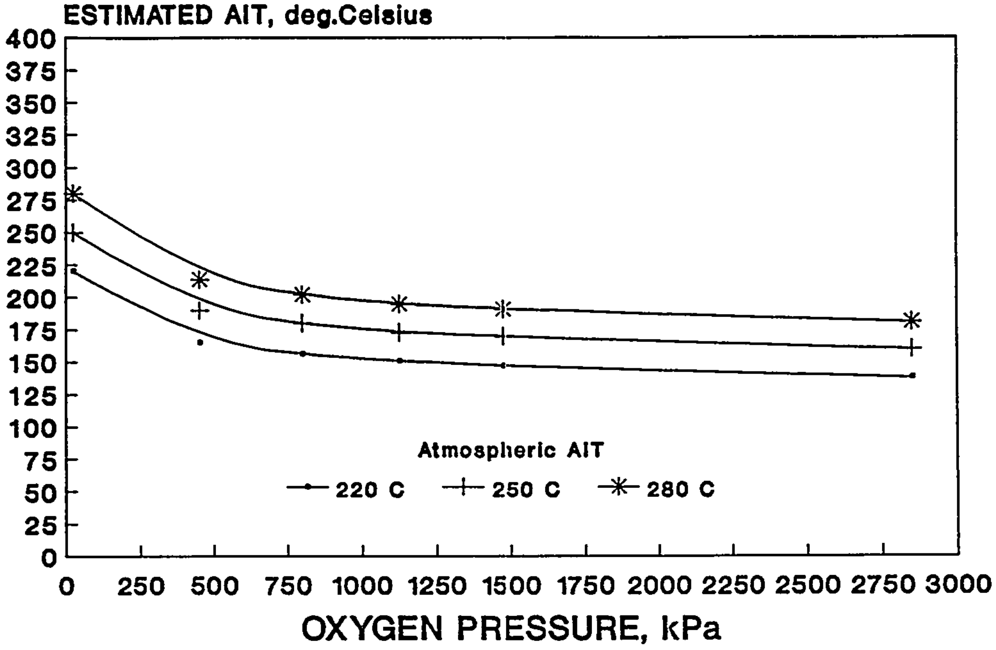

Fig. 1 - Theoretical effect of oxygen pressure on the autoignition temperature of three diesel fuels assumed to have atmospheric AIT levels of 220°, 250°, and 280°C.

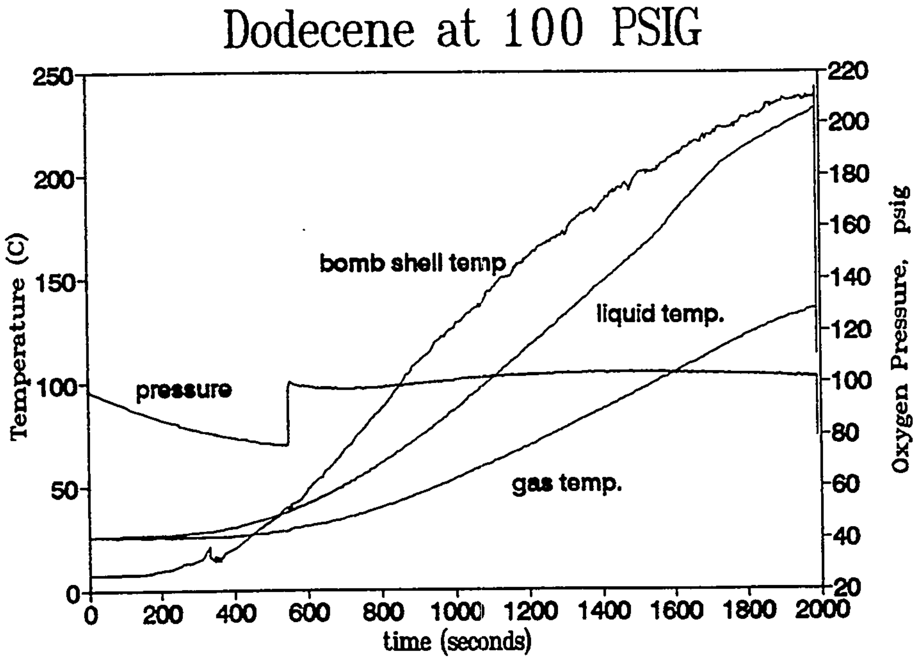

Fig. 2 - Results of AIT screening test on dodecene under 100 psig (800 kPa) and test temperatures up to 225°C; pressure and temperature variations with duration of test.

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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, physical properties, and stability. All data was statistically analyzed, and a multi-variable regression analysis was performed to determine predictive equations for stability and cold flow test results. The statistical analysis 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, and poly-aromatics were identified as important contributors to insolubles formation. 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. Under the most stressful conditions used, average hydroperoxide formation rates for LS and HS fuels had regression equations that differed only by a constant factor. Compositional variables that contributed to secondary and benzylic carbons were found to strongly increase hydroperoxide formation. Examination of the test data also indicated that LS diesel fuels might be less responsive to cold flow improvers than HS diesel fuels.

INTRODUCTION

Before October 1993, No. 2 distillate fuel sold in the United States contained 0.2-0.4 %(wt) sulfur[1-3]. As of October 1993, No. 2 distillate fuel used for on-highway vehicles was required to have a sulfur level no greater than than 0.05 %(wt), i.e. 500 ppm(wt)[4-5]. 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 stability[6-8], 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. This is because of two compositional changes that may occur in diesel fuels with increasing hydrotreating severity[8]:

1. A decrease in natural peroxidation inhibitors.
2. A partial saturation of multi-ring aromatics to produce increased levels of carbons more prone to peroxidation.

The concern over increased levels of hydroperoxides in low sulfur diesel fuel stems from problems observed in some jet fuels over the last thirty years[9-11]. Hydroperoxides have been shown to degrade elastomers in jet aircraft fuel systems. In all such documented cases jet fuels had been hydrotreated, and fuel hydroperoxide levels were 1-8 milli-equivalents active oxygen per kilogram fuel (meq O/Kg)[14]. A later study showed that hydroperoxide susceptibility increased by a factor of 1,000 when a jet fuel was hydrotreated[12]. These observations led to the current military specification requiring all hydrotreated jet fuels to contain antioxidants[13-14], and limiting initial peroxide number to less than 1 meq O/Kg.

A few studies concerning the effect of hydrotreating on No. 2 diesel fuel peroxidation tendency have been published to date[7-8]. One study found that high sulfur diesel fuel samples taken from the field had no measurable hydroperoxides. Researchers concluded that high sulfur diesel fuel was stable with respect to hydroperoxide formation. The study also observed that initial hydroperoxide levels in fresh low and high sulfur diesel fuel were essentially zero. However, low sulfur diesel fuel was much more susceptible to form hydroperoxides under accelerated storage conditions. Five of thirteen low sulfur diesel fuel samples developed hydroperoxide levels ranging from 5.1 to 304 meq O/Kg[8]. This increased hydroperoxide susceptibility did not correlate with increased storage instability (sediment formation/color darkening); all low sulfur diesel fuels had excellent storage stability as measured by the reliable ASTM D4625 (13 week, 43°C, 1 atm. air) procedure. Another study showed that hydrotreated diesel fuels exhibited increased oxygen uptake, and that this tendency became more pronounced as the severity of hydrotreatment was increased[7].

Cold flow behavior is another area that could be impacted by the increased hydrotreating of low sulfur diesel fuels. It has been shown that fuel response to cold flow improver additives can be dependent on the aromatic character of the fuel. Reduced aromatic content of fuel can decrease the performance of a given cold flow improver additive[15]. However, little work has been reported comparing cold flow properties of commercial U.S. low and high sulfur diesel fuels.

The primary objective of the work reported in this paper was to compare the storage stability, hydroperoxide susceptibility, and cold flow properties of a large number of low and high sulfur No. 2 diesel fuels throughout the United States. A secondary objective was to examine changes in fuel composition and physical properties that occur during sulfur level reduction, and determine how those changes correlate with the stability and cold flow properties that are shown to vary significantly between low and high sulfur fuels.

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, physical properties, and stability using the following procedures:

Chemical Composition

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

Physical Properties

Initial Color (ASTM D1500)
API Gravity (ASTM D287)
Distillation (ASTM D86)
Cloud Point (ASTM D2500)
Pour Point (ASTM D97)

Stability

Storage Stability (ASTM D4625)
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. Initial color 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 fuels[16] 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[17]. The procedure involves heating a 50 ml fuel sample at 100°C and 690 kPa (100 psia) O_2 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[18-19], and the procedure for measuring them has been previously documented[20]. Mass spectrometric analysis was based on the Robinson procedure as reported elsewhere[21-22].

Statistical Treatment of Data

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

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

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. Finally, multi-variable regression analysis was performed to determine if fuel composition and physical properties could be correlated with stability and cold flow properties.

Test data for LS and HS diesel fuels were graphically displayed using a format commonly called box plots. For a given test property, each LS and HS fuel value was plotted along a vertical scale (y-axis) with LS test values appearing to the left of HS test values. For data points that overlay each other, the points were "jittered" so as to make them visually distinct. In this way, a visual display of the entire data distribution for LS and HS values was made apparent. For both LS and HS test values, a box was drawn around the central points that comprise one-half of the total data points. Each box was further divided by a single horizontal line at the exact median of the data distribution. At the top of each distribution was given the mean test value and standard deviation. The confidence level (in percent) that the mean LS test value and mean HS test value is different was also given. 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. Box plots of the data are displayed in Figures 1-8. None of the LS fuels significantly exceeded the 500 ppm(wt) maximum allowed value for sulfur. Two of the HS fuels had sulfur levels that were outliers, significantly lower than the remaining distribution. Sulfur and nitrogen values reflected the already demonstrated fact[7] 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. Implications of this result are discussed below in the section dealing with multi-variable regression analysis. The mass spectrometric data indicated that the main statistically significant compositional difference between LS and HS diesel fuels was a partial saturation of poly-aromatic rings. While LS fuels had more mono-aromatics and less poly-aromatics than HS fuels, they did not have significantly less total aromatics. The small but significant reduction in mean molecular weight in LS fuels was probably due to the reduction in sulfur and nitrogen-containing compounds.

Physical Properties

Results of the statistical analysis of physical property tests are given in Table II. Box plots of the data are displayed in Figures 9-17. The mean initial color of LS diesel fuel was about 1.0 ASTM. Dyed fuel made it impossible to determine the mean color for the HS samples. However, based on other data[1] it appeared that LS diesel fuel was somewhat less colored than HS fuel. This is consistent with previously documented work indicating the effect of hydrotreating on diesel fuel color[7,23]. The density of LS diesel fuel as measured by API Gravity decreased by a slight but statistically significant amount compared to HS diesel fuel. This result was consistent with the mass spectrometric data showing a significant partial saturation of poly-aromatics (higher density) to mono-aromatics (lower density). Removal of sulfur and nitrogen-containing compounds also contributed. Distillation data for LS and HS diesel fuel showed small but statistically significant differences for IBP, T50, and T90. The lower T50 and T90 results for LS diesel fuels probably reflect the removal of heavy tails from the hydrotreater feed streams. Refiners often make such cuts so as to more easily achieve the sulfur level targets in the product streams. (The sulfur-containing compounds in diesel fuel that are most difficult to remove by hydrotreating are in the highest boiling fraction of the fuel.) The slightly increased T10 for LS diesel fuel compared to HS diesel fuel may reflect an effort to ensure that flash point specifications are met.

The difference between mean cloud and pour points indicated that cold flow improver additives (pour point depressants) were typically present in LS and HS diesel fuels. (Additive-free No. 2 diesel fuel will have a pour point only 2-3°C lower than the cloud point[24]). Cloud point and pour point for LS and HS diesel fuel did not show statistically significant differences. However, LS fuels did seem to indicate a moderate trend (C.L. = 83.6) towards slightly higher (2°C) pour point. This agrees directionally with the mass spectrometry data. As already mentioned, cold flow improver additives can have decreased effectiveness when diesel fuel aromaticity decreases. Further discussion on pour point, fuel composition, and cold flow improver effectiveness is given below in the section dealing with correlation analysis.

Stability

Results of the statistical analysis of stability tests are given in Table III. Box plots of the data are displayed in Figures 18-22. ASTM D4625 storage stability of all fuels was generally acceptable. Only five of the twenty-six HS fuels (19%) and two of the sixty-nine LS fuels (3%) had total insoluble levels exceeding 1.0 mg/100 ml. 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 improves[1,8]. 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 thing[7].

Hydroperoxide analysis of the diesel fuels yielded interesting results. All fuels except one LS fuel gave zero initial hydroperoxides via the ASTM D3703 titrametric procedure. As already mentioned, 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 formation[8]. 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. Of course, this conclusion is restricted to the LS diesel fuels in the United States during the sampling period. It remains to be determined if the same results would be obtained in LS samples taken during summer months.

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 O_2), 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 mechanism[25]. Very often, a slow initial stage of fuel oxidation, the induction period, occurs after which a more rapid rate of hydroperoxide formation is observed[26-27]. 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.

This is exactly what appears to be occurring in the ninety-five diesel fuels of this study. Under the mildest incubation conditions, ambient commercial transport and storage, the induction period of all but one fuel was not exceeded. Hydroperoxide levels were accordingly zero. As fuels were increasingly stressed, their inherent differences in hydroperoxide susceptibilities became apparent. Finally, it should be remembered that the final hydroperoxide level of a fuel represents the difference in the rate of formation and degradation of hydroperoxides. The average HS diesel fuel hydroperoxide level after the more severe CRC incubation was less than after the less severe ASTM D4625 incubation. This indicates that HS fuels may have typically contained hydroperoxide decomposers that peaked in effectiveness within the severity conditions spanned by the ASTM D4625 and CRC procedures. A similar trend was not observed in the LS fuels.

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. The one obvious circumstance where this could possibly occur is during vehicular use. Typically, in U.S. diesel-powered vehicles, 20-90% of the fuel pumped to the engine is returned to the fuel tank, depending on whether the engine is operating at idle, full throttle, or some intermediate setting. The fuel that is returned is first heated by the engine block. Returned fuel can be warmed by 30°C or more[28]. Depending on how long it takes for a given tank of fuel to be consumed, a LS fuel might eventually develop a measurable increase in hydroperoxides. However, under most on-highway driving conditions, such a scenario may be unlikely. Typically, over the road diesel-powered vehicles consume a tank of fuel in six hours or less. The ASTM D4625 temperature of 43°C required three months to develop a 83.9% confident difference in hydroperoxides between LS and HS fuels. The CRC temperature of 65°C required four weeks, and the OP temperature of 100°C required 24 hours to develop their respective differences in hydroperoxide levels. Although the likelihood of increased fuel tank hydroperoxides due to LS diesel fuel seems remote, additional vehicle tests would be needed to settle the issue.

Multi-variable Regression Analysis

The results of the multi-variable regression analysis of the entire data pool are given in Tables IV-VII. The regression program hunted for the best fit using all compositional variables, API Gravity, and distillation parameters. No attempt was made to separate any variable inter-dependencies that might have existed. The program did determine if a superior model could be found by treating LS and HS fuels separately. If so, the separate regression equations for LS and HS fuels were calculated. Otherwise, the single best-fit regression equation for the entire fuel set was calculated. For each regression equation, the confidence level for each identified variable was tabulated. Overall correlation values (r) and root mean square errors (rmse) for each equation were also calculated.

As indicated in Tables IV-V, weak models for predicting ASTM D4625 total insolubles and CRC Hydroperoxide Potential were found, although the identified variables generally had very high confidence levels. This indicates that there were "missing variables" not in the original set that significantly affected total insolubles and CRC Hydroperoxide Potential. The most important variables identified in the ASTM D4625 total insolubles regression equation were poly-aromatic terms. This is in agreement with recent theories concerning diesel fuel storage instability chemistry[29-30]. Interestingly, the best-fit models were not sensitive to whether the fuel was LS or HS.

SMORS was not identified as a significant variable in the regression equations for any of the stability tests, even though previously reported work has indicated a link[19-20]. For the ASTM D4625 total insolubles regression equation, the SMORS dependence may be implicitly indicated in the poly-aromatic terms, since the structures most commonly attributed to SMORS are multi-ring aromatic condensation products[31]. However, as discussed earlier, SMORS levels did not appear to be significantly different between LS and HS fuels. Since it has been shown that multi-ring aromatics are greatly reduced in LS diesel fuels, the continued presence of SMORS in LS fuels is interesting. Also, SMORS have been linked to ASTM D4625 final color results in HS diesel fuels[32]. Yet, they do not appear to correlate with ASTM D4625 final color in this study, given the LS fuel results. Several questions are suggested by these observations. Does the hydrotreating typically used to produce LS diesel fuel significantly reduce SMORS, or does it merely form more saturated and less reactive species that are still measured as SMORS? If reactive SMORS survive the hydrotreating process used to produce LS diesel fuel, does the hydrotreating remove other co-reactants necessary to trigger the sediment-adverse effect of SMORS (such as sulfur-containing sulfonic acid precursors, for instance[33])? If SMORS are reduced by hydrotreating, do they reform in the resulting LS diesel fuel? If SMORS do reform, what are the kinetics of the process, and are the newly-formed SMORS of the same structural family as the previously- present SMORS? Additional work will be required to answer these questions.

As indicated in Table VI, a moderately strong model was developed for Hydroperoxide Potential by the OP procedure. A separate correlation equation was developed for LS and HS fuels. Most interestingly, the two equations were different by only a constant factor. This strongly suggests that the mechanism for peroxidation under the OP conditions is the same for LS and HS fuels. Also, it suggests that the difference in peroxidation susceptibility between LS and HS fuels is due to some reasonably consistent difference in composition that is parametrically related to fuel sulfur level. This is exactly what would be expected if LS fuels had reduced levels of natural antioxidants and increased levels of more oxidation-prone hydrocarbons. As indicated in the variable analysis, cyclo-paraffins and mono-aromatics strongly impacted OP Hydroperoxide Susceptibility. This is consistent with the fact that secondary (cyclo-paraffins) and benzylic (mono-aromatics formed by partial saturation of poly-aromatics) carbons are more prone to peroxidation. Also, as postulated elsewhere, a reduction in poly-aromatics (implicit in the mono-aromatic trend) may account for some of the reduction in natural antioxidant properties of LS diesel fuels[8].

It is interesting that the less severe CRC Hydroperoxide Potential test did not show this kind of correlation, even though the confidence level of difference between LS and HS fuels was almost as high for the CRC procedure (99.2%) as it was for the OP procedure (99.9%). The implications of this observation with respect to the effect of temperature and oxygen partial pressure on diesel fuel peroxidation is provocative.

As indicated in Table VII, neither cloud point nor the difference between cloud and pour points gave a strong model using the existing variable set, although all identified variables had very high confidence levels. As already mentioned, this indicates that important variables are missing from the variable set. The most likely missing variable for cold flow properties was the cold flow improver additive. The cold flow additive (or additives in the case of diesel fuels taken from fungible shipments) and its concentration will have a profound effect on the amount by which the pour point is depressed below the cloud point. Furthermore, for any given cold flow improver, additive effectiveness is strongly dependent on fuel compositional parameters such as wax content, mean wax molecular weight, wax molecular weight distribution, and fuel aromaticity[15,34]. Nonetheless, variables that were identified as important are at least directionally consistent with previously established principles of distillate cold flow properties. Specifically, the effects of IBP, T90, and two-ring aromatics in the regression equations are consistent with the known effects of wax content and fuel aromaticity on cold flow improver effectiveness.

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. Multi-variable regression analysis for ASTM D4625 total insolubles did not yield a strong model. However, poly-aromatic terms were identified as important in diesel fuel insolubles formation. SMORS were not identified explicitly as a variable affecting insolubles formation, but may have been included as part of the poly-aromatic terms. Even so, mean SMORS levels were not statistically different for LS and HS diesel fuels. The effect of hydrotreating processes used to produce LS diesel fuel on SMORS, and the effect of SMORS on LS and HS diesel fuel instability need further clarification.

4. 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.

5. Multi-variable regression analysis indicated that at the most severe test conditions used (100°C, 24 hours, 690 kPa O_2), LS and HS diesel fuels generated hydroperoxides by the same mechanism, but with an average rate that was less for HS fuels by a constant factor. Compositional variables that contributed to secondary and benzylic carbons were found to strongly increase hydroperoxide formation, as previously suggested in the literature.

6. All diesel fuels contained cold flow improver additives to depress the pour point. Overall data indicated a moderate trend toward somewhat lower pour point in HS fuels compared to LS fuels. This was paralleled by the observed differences in aromatic profile for LS and HS fuels. The regression equations for cold flow properties were not strong, indicating the importance of the cold flow additive itself. However, the variables that were identified did agree directionally with compositional factors known to affect cold flow additive performance. This may indicate that LS diesel fuels may be somewhat less responsive to currently used cold flow additives than HS diesel fuels.

ACKNOWLEDGMENTS

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REFERENCES

1. Amoco Corporation. Unpublished data.

2. Dickson, C. L.; Woodward, P. W. "Diesel Fuel Oils, 1990," NIPER-167 PPS-90/5, October 1990.

3. "Worldwide 1993 Winter Diesel Fuel Quality Survey," Paramins.

4. *Federal Register* (CFR Pars 80 and 86) Vol. 55, No. 162, pp 34120ff, 8/21/90.

5. Clean Air Act Amendments of 1990, House of Representatives Report #101-952, 10/26/90.

6. Palmer, L. D.; Copson, J. A. "Hydrotreatment of Light Cycle Oil for Stabilization of Automotive Diesel Fuel," Proceedings of 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, July 1986.

7. Martin, B.; Bocard, C.; Durand, J. P.; Bigeard, P. H.; Denis, J.; Dorbon, M.; Bernasconi, C. "Long-Term Storage Stability of Diesel Fuels: Effect of Ageing on Injector Fouling; Stabilization by Additives or Hydrotreating," presented at SAE Fuels and Lubes meeting, Tulsa, Oklahoma, 1990.

8. Vardi, J.; Kraus, B. J. "Peroxide Formation in Low Sulfur Automotive Diesel Fuels," SAE Paper No. 920826, 1992.

9. Smith, M. *Aviation Fuels,* G. T. Foulis & Co., Ltd., Henley-on-Thames, England, 1970, chapter 51.

10. Shertzer, R. H. "Aircraft Systems Fleet Support/Organic Peroxides in JP-% Investigation," Final Report NAPC-LR-78-20; Naval Air Propulsion Center, Trenton New Jersey, 1978.

11. Fettke, J. M. "Organic Peroxide Growth in Hydro-treated Jet Fuel and its Effect on Elastomers," GE TM83AEB1154, General Electric, Lynn, Massachusetts, 1983.

12. Watkins, J. M., et al. "Hydroperoxide Formation and Reactivity in Jet Fuels," *Energy and Fuels* **1989**, *3*, pp 231-236.

13. Military Specification MIL-T-5624P, 9/29/92.

14. Military Specification MIL-T-83133D, 9/29/92.

15. Tiedje, J. L. "The Use of Pour Point Depressants in Middle Distillate Fuels," Proceedings of the Sixth World Petroleum Congress, Frankfurt am Main, June 1963.

16. Determination of the Hydroperoxide Potential of jet Fuels, CRC Report No. 559, April 1988.

17. Black, B. H.; Hardy, D. R. "Comparison of Jet Fuel Phenolic Antioxidants Using A Serial Dilution Technique," Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November 1991.

18. Hardy, D. R.; Wechter, M. A. *Energy and Fuels* **1990**, *4*, 271.

19. Wechter, M. A.; Hardy, D. R. "The Use of Macromolecular Oxidatively Reactive Species (SMORS) to Predict Storage Stability of Mid-Distillate Diesel Fuels," Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November 1991.

20. Hardy, D. R.; Wechter, M. A. "What Are Soluble Macromolecular Oxidatively Reactive Species (SMORS)?" ACS National Meeting, Washington, D.C., August 1990.

21. Robinson, C. J.; Cook, G. L. *Anal. Chem* **1969**, *41*, 1548.

22. Robinson, C. J. *Anal. Chem.* **1971**, *43*, 1425.

23. Takatsuka, T.; Wada, Y.; Suzuki, H.; Komatsu, S.; Morimura Y. "Deep Desulfurization of Diesel Fuel and its Color Degradation," *J. Jpn. Petrol. Inst.* **1992**, *4*(2), pp 179-184.

24. Deen, H. E.; Kaestner, A. M.; Stendahl, C. M. "Additives to Improve Quality and Low Temperature Handling of Middle Distillate and Residual Fuels," Proceedings of the Seventh World Petroleum Congress, 1967.

25. Lundberg, W. O. (Ed.) *Autooxidation and Antioxidants.* Interscience (John Wiley and Sons), 1961.

26. Fodor, G. E.; Naegali, D. W.; Kohl, K. B. "Peroxide Formation in Jet Fuels," *Energy and Fuels* **1988**, *2*, pp 729-734.

27. Fodor, G. E.; Naegali, D. W. "Peroxide Formation in Jet Fuels," presented at ACS National Meeting, Washington D.C., August 1990.

28. Muzatko, J. W. "Reducing Low Temperature Wax Plugging in Fuel Systems of the Diesel Passenger Car," SAA Paper No. 800222, February 1980.

29. Pedley, J. F. "The Chemistry of Sediment Formation During the Storage of Diesel Fuel," PhD. Thesis, University of London, 1988.

30. Tort, F.; Waegell, B.; Bernasconi, C.; Germanaud, L. "Mechanistic Aspects of Oxidation Processes Involved in Colour and Sediment Formation During Aging of LCO Containing Fuels," Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November 1991.

31. Malhotra, R. "Field Ionization Mass Spectrometric Analysis of Sediments: Chemistry of Insolubles Formation," Proceedings of the 4th International conference on Stability and Handling of Liquid Fuels; Orlando, Florida, November 1991.

32. Waynick, J. A. "Evaluation of Commercial Stability Additives in Middle Distillate Fuels," Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels; Rotterdam, the Netherlands, October 1994.

33. Hazlett, R. N. "Acid Base Phenomena in Distillate Fuel Stability," *Fuel Sci. and Tech. Int'l.* **1988**, *6*(2), pp 185-208.

34. Knepper, J. I.; Hutton, R. P. "The Cold Flow Properties of Distillate Fuels: The Effect of n-Paraffins in Distillate Fuels and Their Response to Cold Flow Improver Additives," presented at the National Fuels and Lubricants Meeting, Houston, Texas, September 1975

Figure 1
U.S. Low versus High Sulfur Middle Distillate Fuels
Sulfur, ASTM D4294

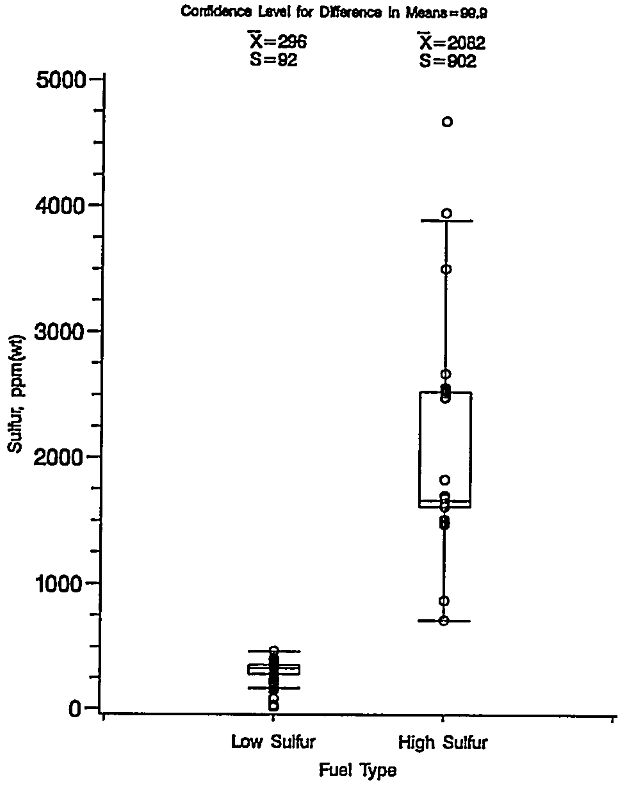

Figure 2
U.S. Low versus High Sulfur Middle Distillate Fuels
Nitrogen, ASTM D4629

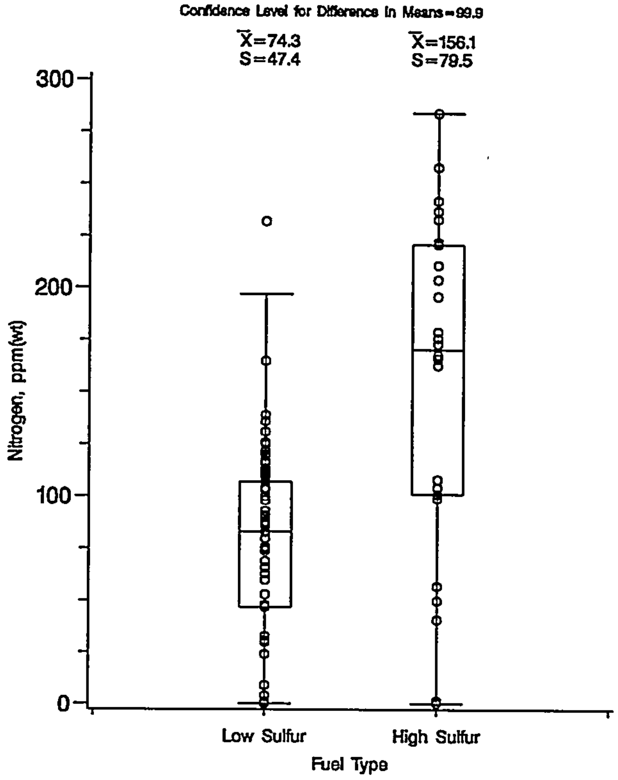

Figure 3
U.S. Low versus High Sulfur Middle Distillate Fuels
SMORS

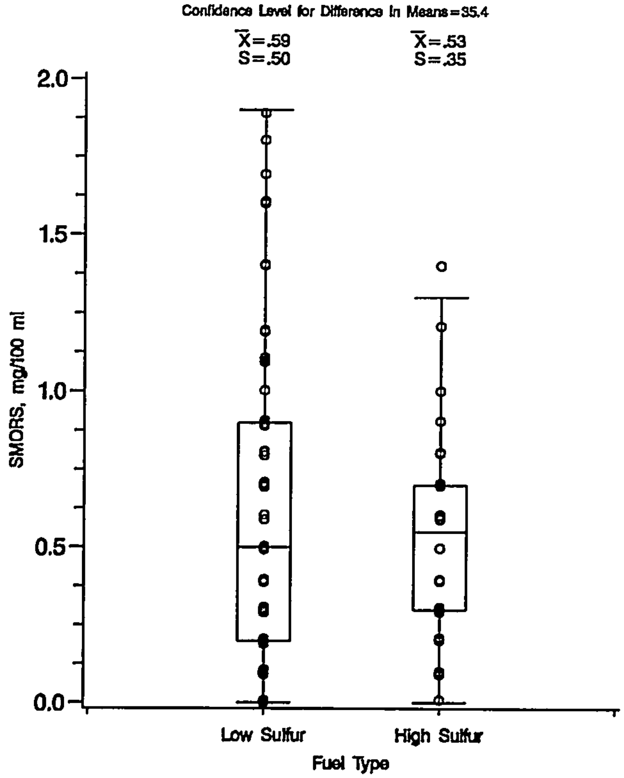

Figure 4
U.S. Low versus High Sulfur Middle Distillate Fuels
Total Saturates by Mass Spectrometry

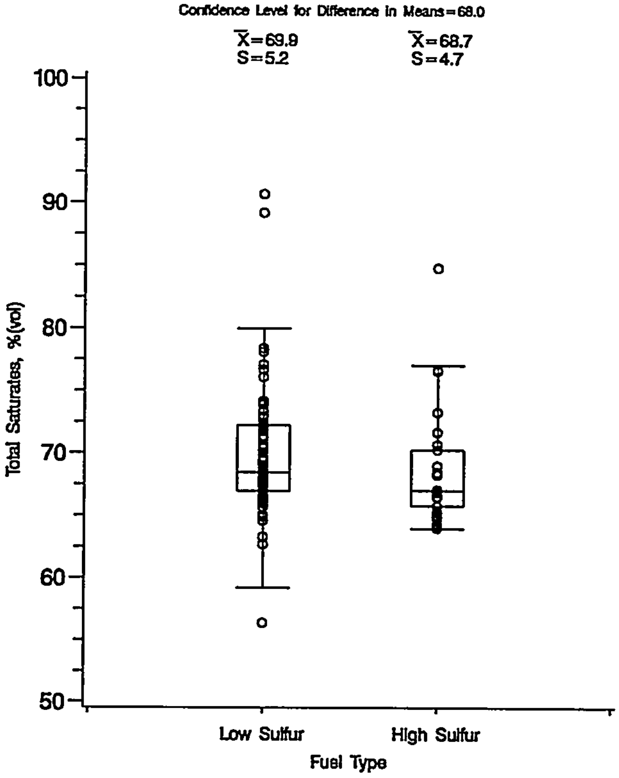

Figure 5
U.S. Low versus High Sulfur Middle Distillate Fuels
Total Aromatics by Mass Spectrometry

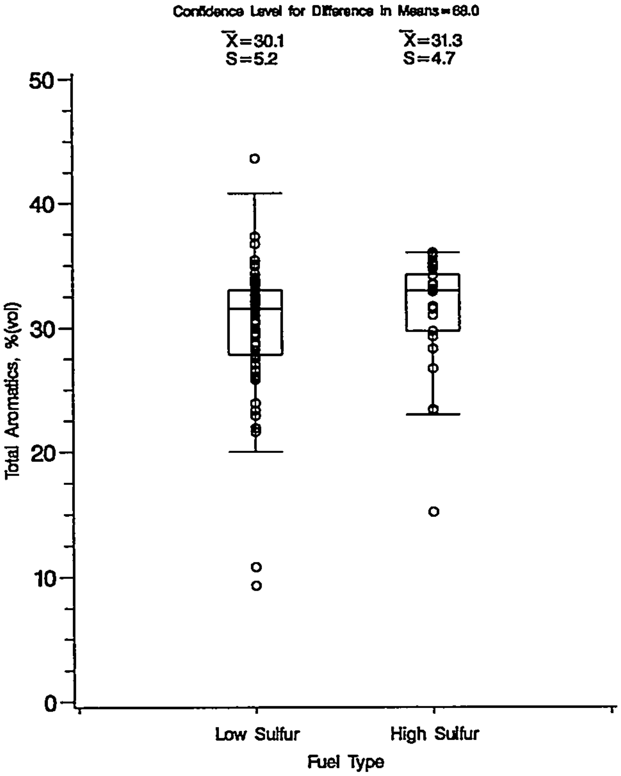

Figure 6
U.S. Low versus High Sulfur Middle Distillate Fuels
Mono–Aromatics by Mass Spectrometry

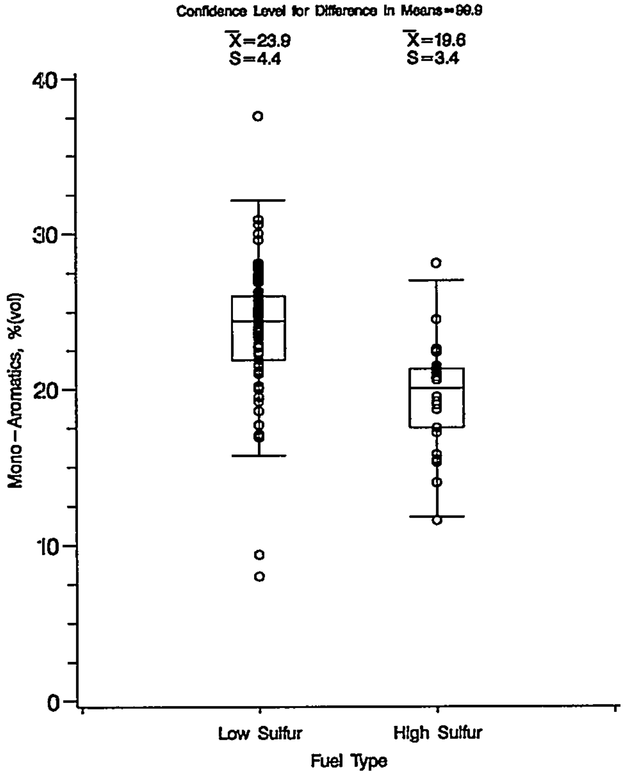

Figure 7
U.S. Low versus High Sulfur Middle Distillate Fuels
Poly–Aromatics by Mass Spectrometry

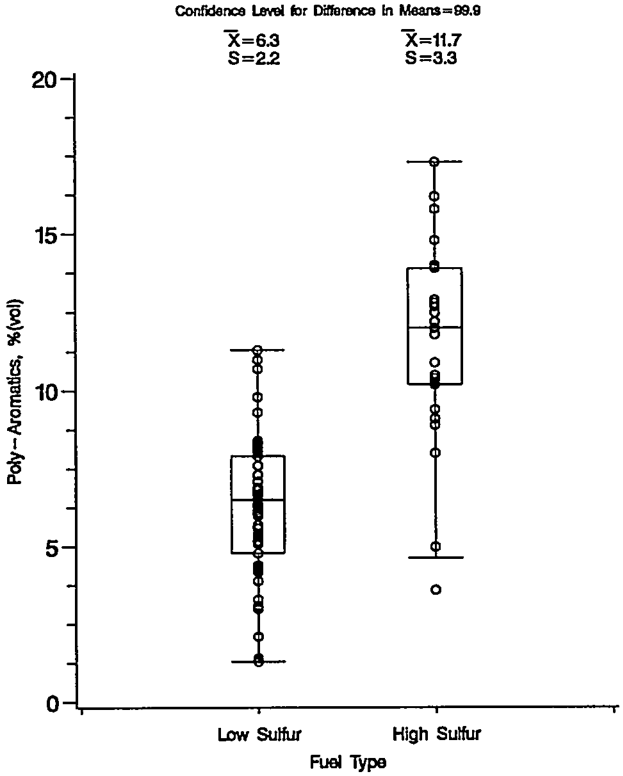

Figure 8
U.S. Low versus High Sulfur Middle Distillate Fuels
Mean Molecular Weight by Mass Spectrometry

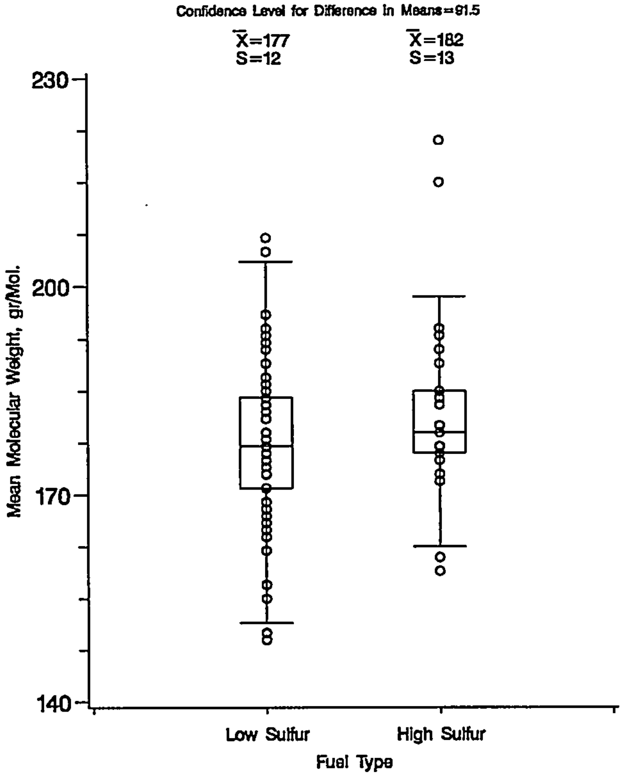

Figure 9
U.S. Low versus High Sulfur Middle Distillate Fuels
Initial Color, ASTM D1500

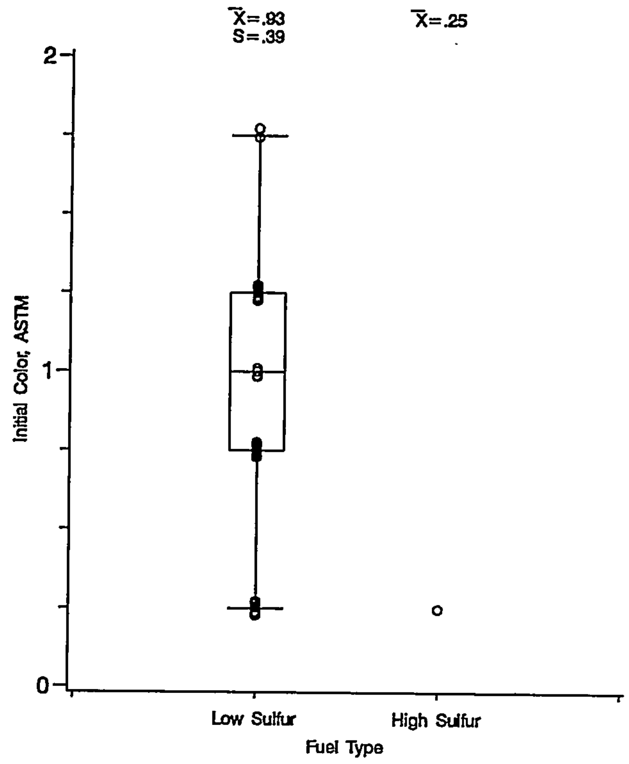

Figure 10
U.S. Low versus High Sulfur Middle Distillate Fuels
API Gravity, ASTM D287

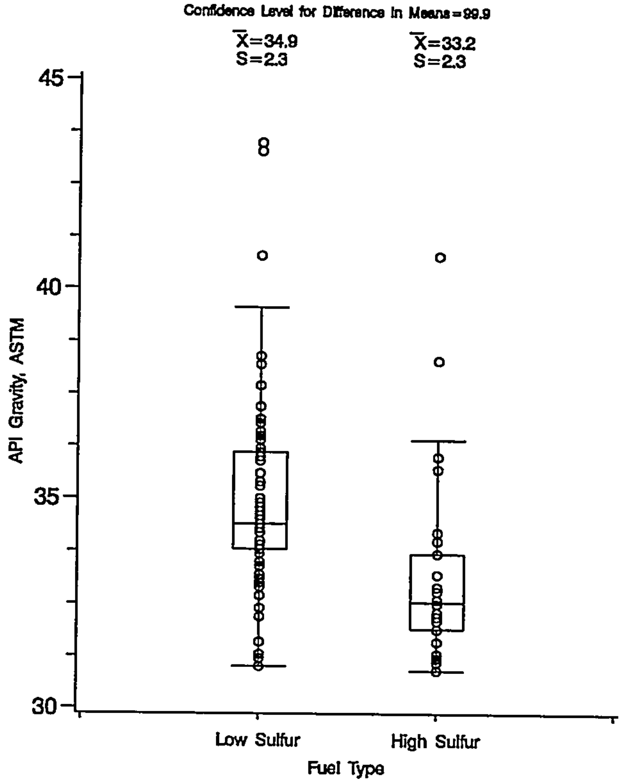

Figure 11
U.S. Low versus High Sulfur Middle Distillate Fuels
Initial Boiling Point, ASTM D86

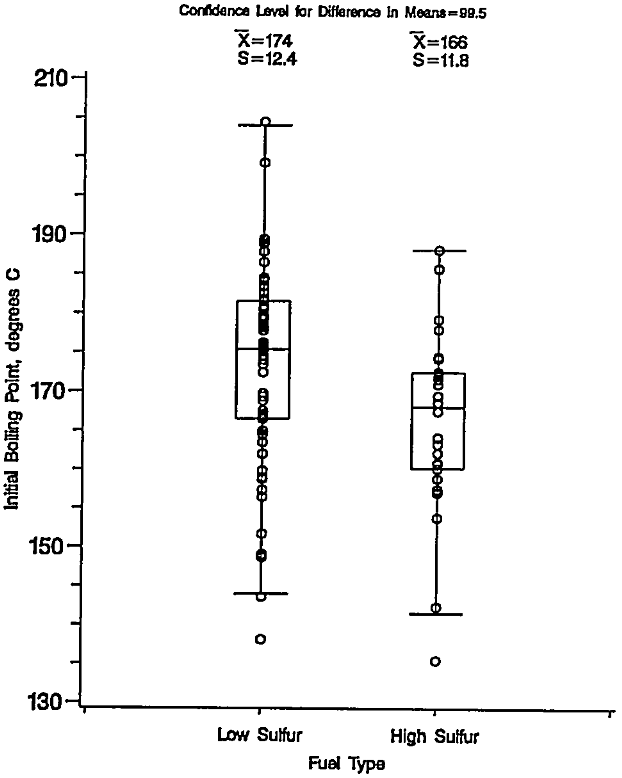

Figure 12
U.S. Low versus High Sulfur Middle Distillate Fuels
10% Recovery Temperature, ASTM D86

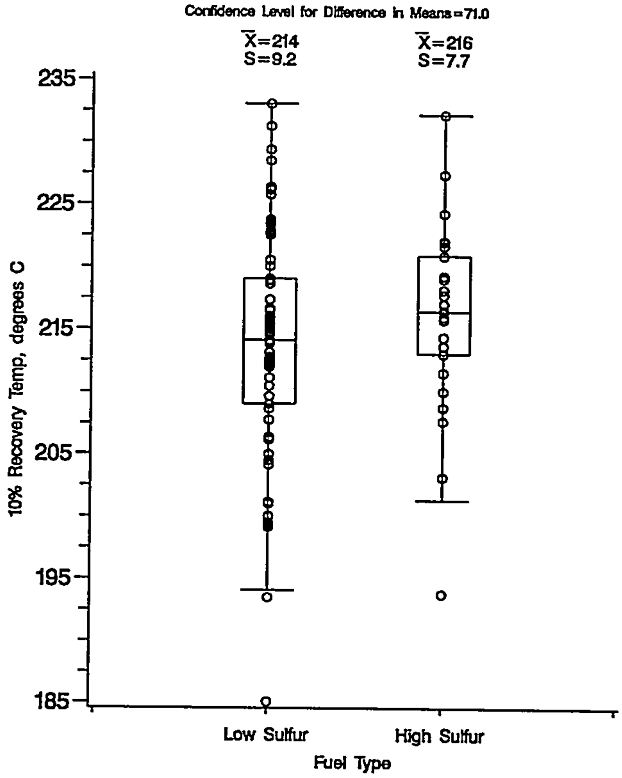

Figure 13
U.S. Low versus High Sulfur Middle Distillate Fuels
50% Recovery Temperature, ASTM D86

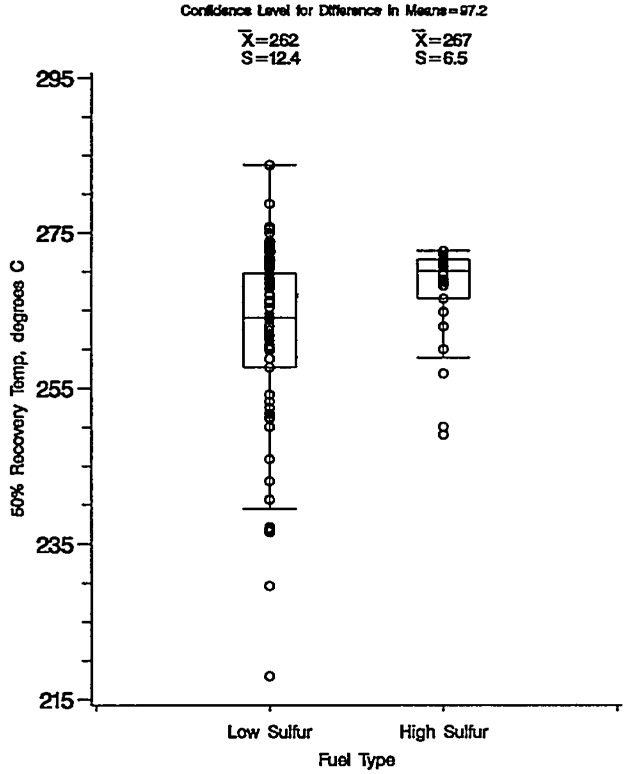

Figure 14
U.S. Low versus High Sulfur Middle Distillate Fuels
90% Recovery Temperature, ASTM D86

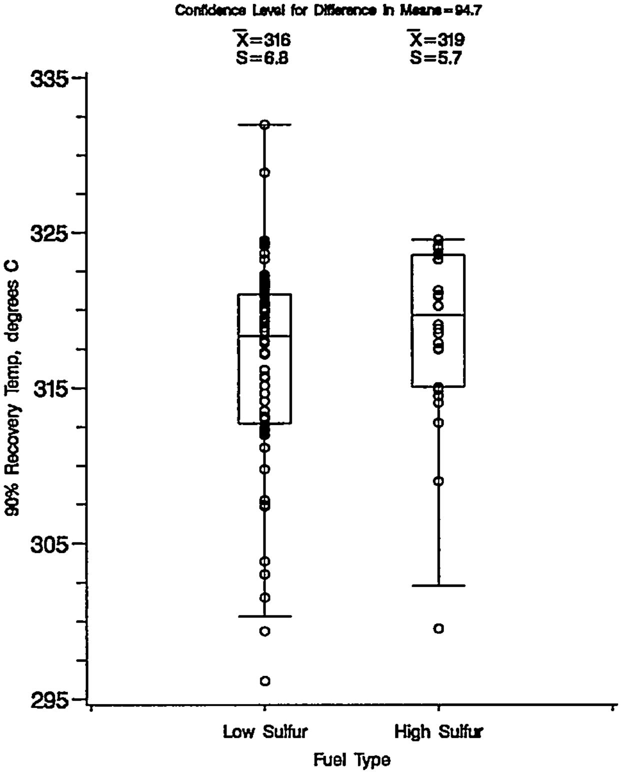

Figure 15
U.S. Low versus High Sulfur Middle Distillate Fuels
Final Boiling Point, ASTM D86

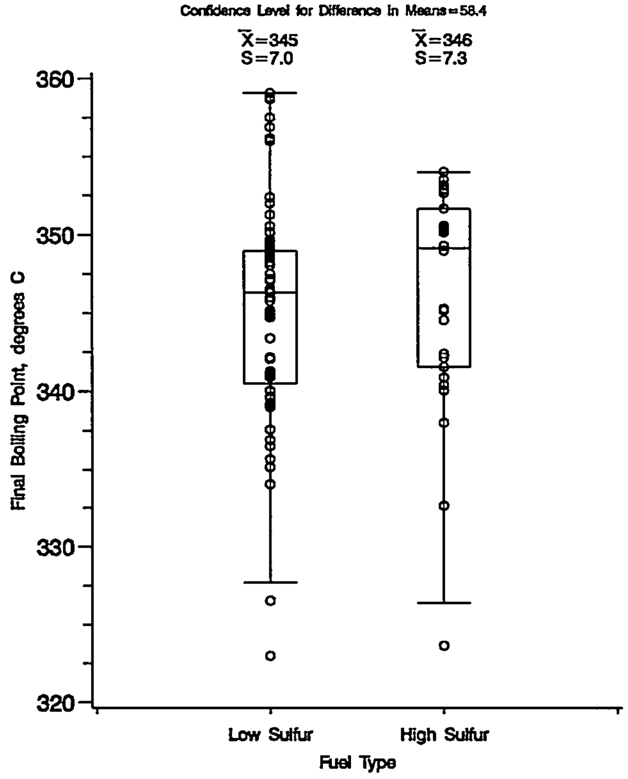

Figure 16
U.S. Low versus High Sulfur Middle Distillate Fuels
Cloud Point, ASTM D2500

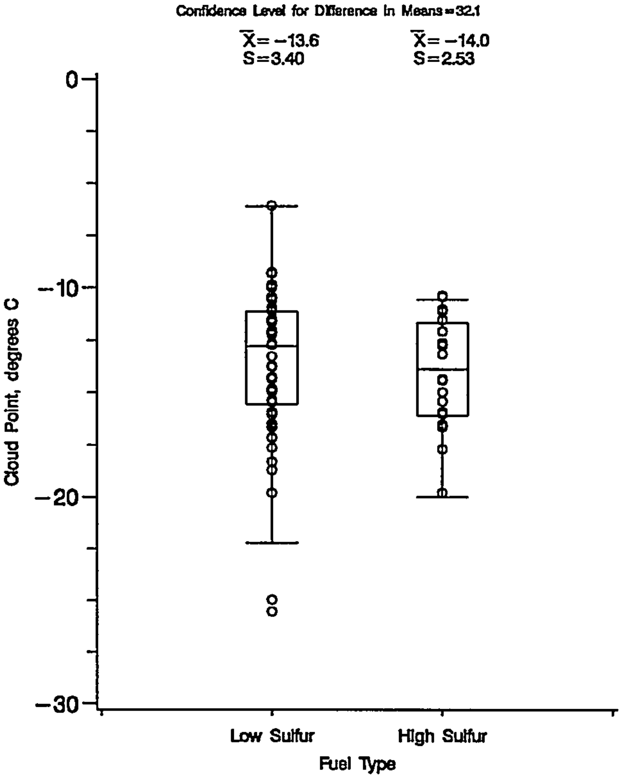

Figure 17
U.S. Low versus High Sulfur Middle Distillate Fuels
Pour Point, ASTM D97

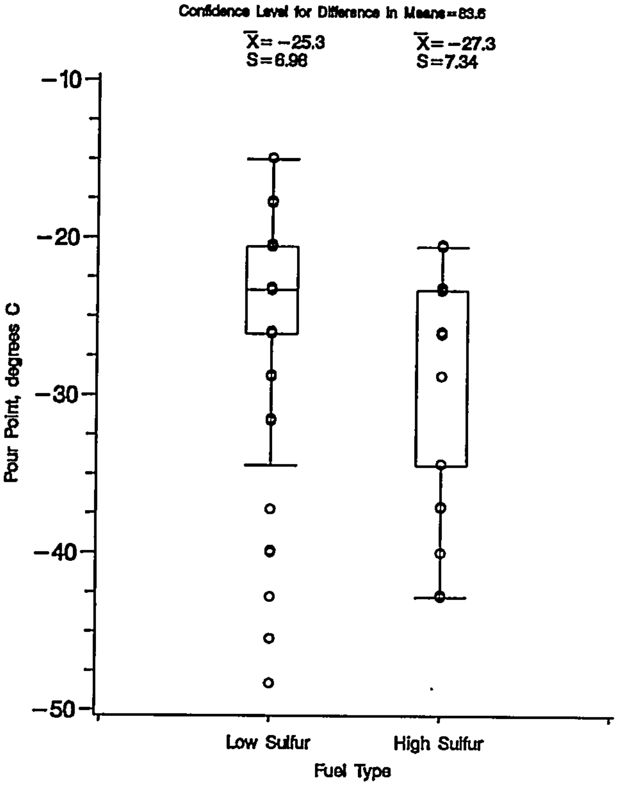

Figure 18
U.S. Low versus High Sulfur Middle Distillate Fuels
Total Insolubles, ASTM D4625

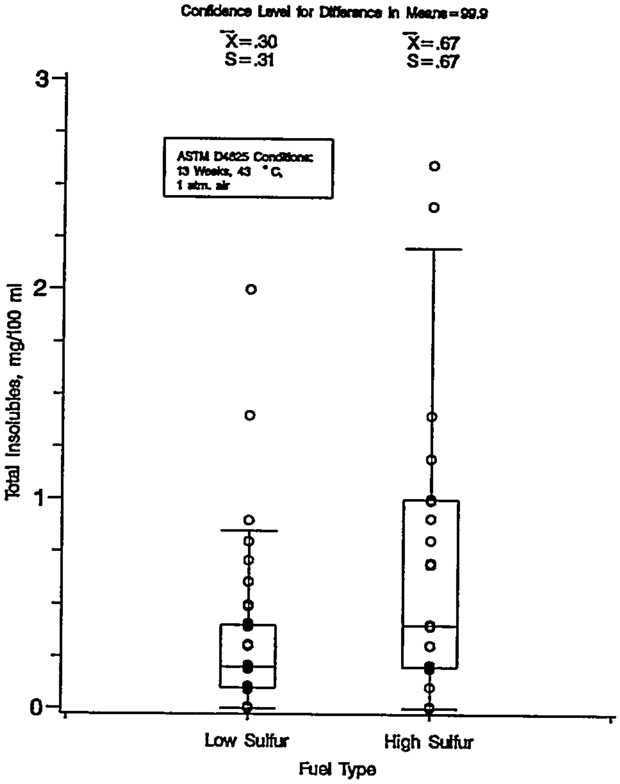

Figure 19
U.S. Low versus High Sulfur Middle Distillate Fuels
Final Color, ASTM D4625

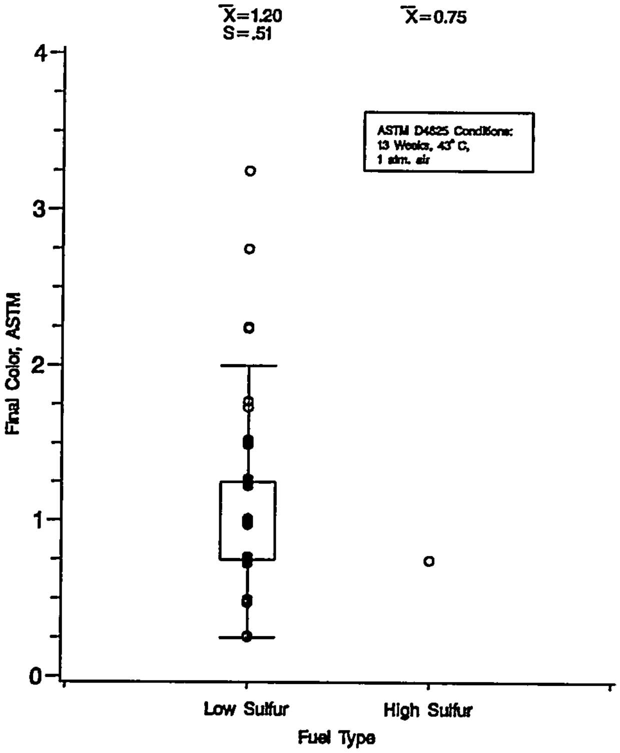

Figure 20
U.S. Low versus High Sulfur Middle Distillate Fuels
Final Peroxide Number after ASTM D4625

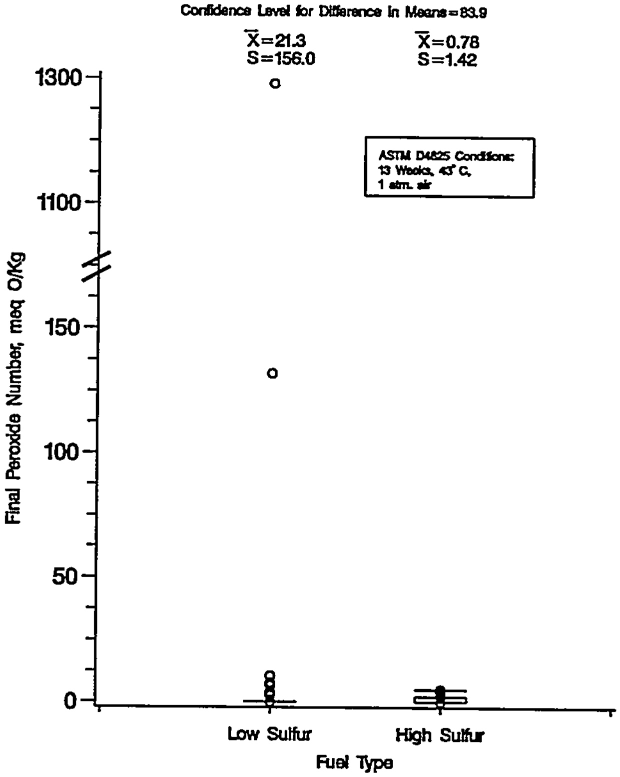

Figure 21
U.S. Low versus High Sulfur Middle Distillate Fuels
Hydroperoxide Potential, CRC

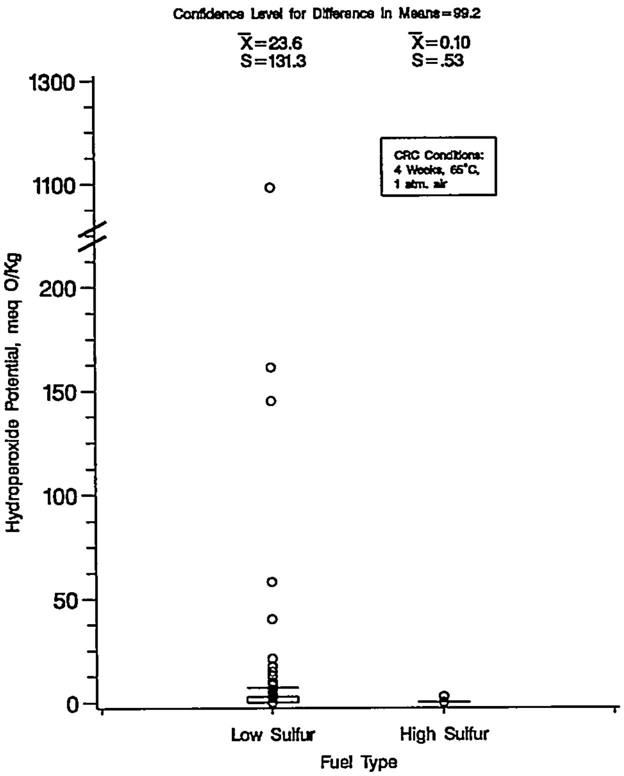

Figure 22
U.S. Low versus High Sulfur Middle Distillate Fuels
Hydroperoxide Potential, Oxygen Overpressure

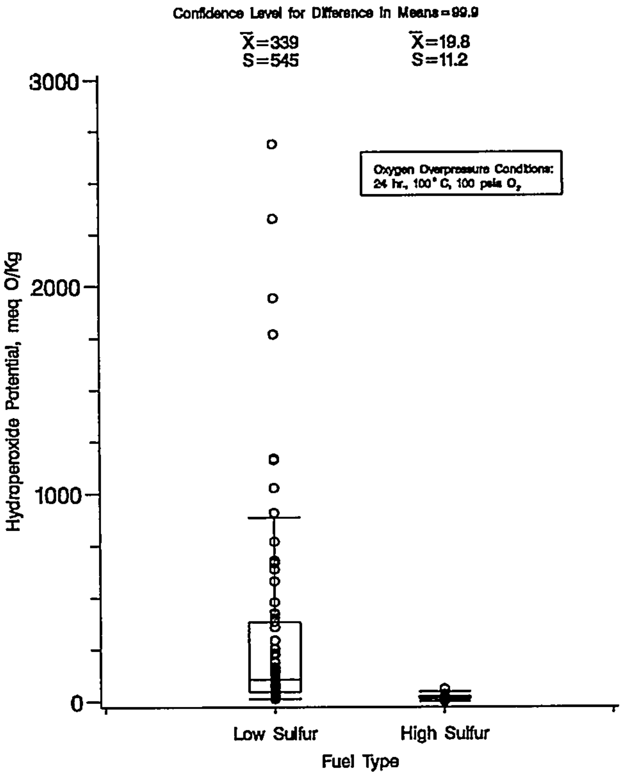

Table I
Results of the Statistical Analysis
Chemical Composition

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
Mean Molecular Weight	177	12	182	13	91.5	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
Physical Properties

Test	Low Sulfur Mean	Low Sulfur St Dv	High Sulfur Mean	High Sulfur St Dv	Conf. Level for Diff.	Test Metric [1]
Initial Color, ASTM D1500	.93	.39	.25 [2]	--	--	Original
API Gravity, ASTM D287	34.9	2.3	33.2	2.3	99.9	Original
Distillation, ASTM D86, °C						
Initial Boiling Pt.	174	12.4	166	11.8	99.5	Original
10% Recovery Pt.	214	9.2	216	7.7	71.0	Original
50% Recovery Pt.	262	12.4	267	6.5	97.2	Original
90% Recovery Pt.	316	6.8	319	5.7	94.7	Original
Final Boiling Pt.	345	7.0	346	7.3	58.4	Original
Cloud Pt., °C, ASTM D2500	-13.6	3.40	-14.0	2.53	32.1	Original
Pour Pt., °C, ASTM D97	-25.3	6.98	-27.3	7.34	83.6	Original

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

Table III
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.

Table IV
Regression Analysis of ASTM D4625 Total Insolubles

Variable	Coefficient	Confidence Level
Intercept	-8.67	--
Initial Boiling Point (IBP)	-.00664	91.1
10% Recovery Point (T10)	.0245	99.8
API Gravity (API)	.0890	94.2
3-Ring Aromatics (3RAr)	1.08	99.9
4-Ring Aromatics (4RAr)	2.93	97.2
Molecular Weight (MW)	-.0237	99.9

r = .62, rmse = .64

Prediction Equation

TI = Exp{-8.67 - .00664*IBP + .0245*T10 + .0890*API + 1.08*3RAr + 2.93*4RAr - .0237*MW} - .08

Table V
Regression Analysis of CRC Hydroperoxide Potential

Variable	Coefficient	Confidence Level
Intercept	20.1	--
Final Boiling Point (EP)	-.0561	99.6
Mono-Aromatics (MAr)	1.44	99.6
Molecular Weight (MW)	.0661	71.9
MAr*MW	-.00734	99.0

r = .57, rmse = 2.15

Prediction Equation

CRC = Exp{20.1 - .056*EP + 1.44*MAr + .066*MW - .007*MAr*MW} - .04

Table VI
Regression Analysis of Oxygen Overpressure
Hydroperoxide Potential

Variable	Coefficient	Confidence Level
Intercept	-22.6	--
hisulf	-.872	99.9
Initial Boiling Point (IBP)	.0143	99.9
90% Recovery Point (T90)	.0165	92.3
Cyclo-Paraffins (CPar)	.341	99.9
Mono-Aromatics (MAr)	.241	99.9

r = .82, rmse = .88

Prediction Equations

Low Sulfur OP = Exp{ -22.6 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
High Sulfur OP = Exp{ -22.6 - .872 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
= Exp{-.872} * Exp{ -22.6 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
= .418 * Exp{ -22.6 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
= .418 * Low Sulfur OP

Table VII
Regression Analysis of Cold Flow Properties
Pour Point

Variable	Coefficient	Confidence Level
Intercept	-88.8	--
Initial Boiling Point (IBP)	.147	99.6
90% Recovery Point (T90)	.280	98.8
API Gravity (API)	-1.27	99.8
Nitrogen (N)	.037	99.5
2-Ring Aromatics (2RAr)	-1.50	99.9

r = .61, rmse = 5.6

Prediction Equation

Pour Point = -88.8+.147*IBP+.280*T90-1.27*API+.037*N-1.50*2RAr

Cloud Point - Pour Point

Variable	Coefficient	Confidence Level
Intercept	-28.6	--
Initial Boiling Point (IBP)	-.154	99.8
API Gravity (API)	1.72	99.9
Nitrogen (N)	-.031	98.9
2-Ring Aromatics (2RAr)	1.55	99.9

r = .57, rmse = 5.4

Prediction Equation

Cloud Point - Pour Point = -28.6 - .154*IBP + 1.72*API - .031*N + 1.55*2RAr

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CHARACTERIZATION OF SOLUBLE MACROMOLECULAR OXIDATIVELY REACTIVE SPECIES (SMORS) FROM MIDDLE DISTILLATE DIESEL FUELS: THEIR ORIGIN AND ROLE IN INSTABILITY

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Abstract

Compositional characterization of a solid phase material isolated by extraction from filtered liquid phase diesel fuels is reported. This solid phase material (SMORS) is shown to be the product of reactive fuel constituents and intermediate to the formation of fuel insoluble sludge. The composition of this material changes during blending processes and tends to become more oxygen rich and thus more polar. Elemental analysis, average molecular weight and pyrolysis mass spectral data are presented for SMORS from a number of representative blended fuels and their blending stocks. SMORS has been shown to be made up of oxidized trimers, tetramers and possibly higher n-mers of nitrogen containing precursors originally present in the fuel. It is not possible to determine the SMORS precursors in field aged fuel (such as those in this study) since these precursors are essentially depleted from the fuel by the time very small amounts of SMORS have been formed.

Introduction

The search for components in catalytically cracked diesel fuel which can be linked to the production of insolubles as the fuel is subjected to oxidative aging has led to a proposal that these precursors can be isolated from filtered fuels by methanol extraction.[1] It was found that unstable fuels containing cracked stock could be greatly stabilized with respect to insolubles formation by methanol extraction prior to oxidative aging.[2] Moreover, if the methanol extract portion was subsequently dissolved in filtered, oxidatively stable hydrocarbon solvents and aged under the same conditions as the unextracted unstable fuels, remarkable mass balances were achieved for the insolubles formed. Thus, it followed logically that the precursors responsible for oxidative instability in diesel fuels were associated with the methanol extractable fraction of the fuels.

If the methanol is removed from the methanol extract by roto-evaporation or by evaporating in a water bath, a dark colored solid is isolated by precipitation with hexane followed by filtration. For fuels which are at least 6 months past production date, the amount of this Extraction Induced Precipitate (EIP) has been found to correlate well and linearly with insolubles formed by accelerated fuel stability tests. This relationship has been shown over a wide range of fuel instabilities. We have termed the precipitate or insoluble sludge generated by these accelerated tests as Thermally Induced Precipitate (TIP).[3] We have suggested that the presence of this EIP or fuel Soluble, Macromolecular, Oxidatively Reactive Species (SMORS) in these fuels thus accounts for the production of insoluble sediment during oxidative aging of diesel fuels (TIP).[1,3] In this paper the acronym EIP will be used in place of SMORS in most cases.

An intriguing suggestion by Chertkov, et al.[4] is consistent with this theory that proposes the presence of a soluble macromolecular species as a precursor to oxidative instability. They suggest that the product solid phase is not formed by the oxidation of fuel components but is present in the fuel in the form of a colloidal system. Oxidation of the fuel then induces destruction of the colloid and precipitation of the solid phase. They believe that this higher molecular weight material soluble in the fuel causes sludge formation in jet and diesel fuel. They also claim that this material should resemble petroleum asphaltenes except in their (the soluble macromolecules) much higher oxygen incorporation.

Since EIP is contained in the methanol phase, it was originally analyzed by capillary GC and GC/MS. It was later realized that the actual EIP was a macromolecular species and thus not amenable to GC analysis. The methanol phase did contain quite a number of extraneous fuel polars. Many of these such as fluorenes, phenalenes, phenalenones, indoles and quinolines have been implicated by others as likely precursors to instability.[5-9] However, we found no qualitative or quantitative relationship between any of these compound types and stability for any of the test fuels, even though the methanol phase in every case had been explicitly shown to relate to the insolubles formed (TIP). This led to the suggestion that something else in the methanol extract was responsible for TIP/sludge formation, i.e., the extraction induced precipitate, EIP.

During size exclusion chromatographic (SEC) analysis of the methanol fraction the EIP was isolated as described above. This EIP material was very soluble in tetrahydrofuran and upon SEC analysis gave a single broad peak in the molecular weight region of 600 to 900 daltons. This is in the approximate molecular weight range reported for many previous studies on TIP/sludge.[12]

This leads to the questions: what are the EIP; how do they arise; and can their origin and subsequent apparent role be controlled? This work describes and summarizes the characterization studies performed to date on the EIP from representative fuels which are all greater than 6 months past production.

Experimental

All procedures for filtering fuels, and for extraction and precipitation steps used in isolating the EIP from fuels have been described in detail elsewhere.[1,2]

Size-exclusion chromatograms were obtained for the solids using a Beckman-Altex Microspherogel column, Model 255-80 (50 A pore size, 30 cm X 8.0 mm i.d.). A Beckman Model 100-A HPLC pump was used for solvent delivery and a Waters Model 401 differential refractometer was used for detection. Samples were injected using a Rheodyne Model 7125 loop/valve injector, and the recorder was a Varian Model 9176 strip chart. Fisher HPLC grade uninhibited tetrahydrofuran (THF) was used as the mobile phase and weighed samples were dissolved in THF before injection. Molecular weight calibrations were accomplished using polystyrene standards. Flow rates of 1 mL/min were used for all chromatographic work.

GC analysis was performed on samples dissolved in methanol using a Hewlett-Packard Model 5890 GC equipped with flame ionization detector and HP Model 3392 integrator. A 50-m methylated silicone (nonpolar) capillary column was used for separation. Experimental conditions included an inlet temperature of 280 °C, a split ratio of 22:1 and a column temperature program between 100 °C and 280 °C. A 1-min initial hold at 100 °C was used; the temperature was then ramped at 5 °C/min to 280 °C and then held at that temperature for 10 minutes.

Field Ionization Mass Spectrometry (FIMS) involves passing vapors (in this case volatilized pyrolyzates) of the solid material to be analyzed through a region of intense electric field.[10] This mild ionization technique usually results in the formation of only the molecular ions for most compounds, and the absence of fragment ions makes it particularly useful for examining complex mixtures. The FIMS system used for this work has been described elsewhere.[10-11] It consists of an activated tantalum foil field ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. For the pyrolysis FIMS approximately 50 ug of the sample is introduced via a heated direct insertion probe. Mass spectral data of the evolving volatiles are collected by repeatedly scanning the magnet over a preset range while the sample is gradually heated from ambient temperature to about 500° C. The mass range normally scanned is between 90 and 1400 daltons. The mass resolution of the double focussing analyzer is > 30,000 at 300 Da. At the end of the run, the sample holder is retrieved and weighed to determine the fraction that was volatilized during the pyrolysis.

Low voltage electron impact, high resolution mass spectrometry (mass resolution >120,000 at 300 Da) was used to determine the exact masses of several of the key fragment ions, when the EIP was introduced by pyrolysis (similar to the FIMS sample introduction).

Elemental analyses and molecular weight determinations by vapor pressure osmometry were provided by commercial laboratories. All elements including oxygen (but not sulfur) were determined by combustion and not by difference.

All blended stocks used were prepared in the laboratory as 80/20 straight run/LCO mixtures (v/v). Blends were prefiltered before extraction. The straight run fuel used was a water-white, clear stock obtained from the same refinery that furnished LCO-3. All fuels and blends are described in earlier papers in this series[1-3] and a consistent fuel code has been continued.

Results and Discussion

Elemental Analyses/Molecular Weights by Vapor Pressure Osmometry

Table I summarizes the elemental analysis data (CHON) obtained for solids (EIP) extracted from 1 unusual 15 year old straight run distillate, 3 light cycle oils (LCOs) and 5 blends. Data are as received and not normalized to 100%.

The straight run distillate fuel (SR-1) is unusual for 2 reasons. First it is very old and continues a pattern begun about 15 years ago of forming sludge both at ambient and in accelerated tests such as ASTM D5304. As it ages the actual rate of sludge formation has continued to increase. Second, it is very rare for SR distillate streams to form sludge and most SR distillate streams examined to date have very low EIP as a corollary. This SR-1 not only forms sludge but has significant levels of EIP. The EIP of SR-1 is of interest to compare to the EIP of catalytically cracked LCO. (See also the Pyrolysis FIMS section.) Although one might expect the precursors to EIP from the 2 different processing streams to be quite different it is seen that the elemental analysis is quite similar.

The elemental analysis results for 20% LCO/80% SR EIP from blends is shown in the bottom half of Table 1. Here it is interesting to compare the blends to the LCO's. In general the EIP from blends have somewhat higher oxygen and lower carbon content indicating that EIP from <u>blends</u> is more polar than from LCO's. If higher polarity equates to higher chemical reactivity, then this finding supports the long-known fact that blending reactive LCO's with non-reactive SR streams does not usually dilute the sludge forming tendencies in a direct ratio. With very reactive LCO's, dilution by as much as 70% SR sometimes has no effect on reducing sludge formation amounts in the resulting blends.[17] It is noteworthy that these blends are made up immediately before the EIP is isolated for elemental analysis and thus the chemical changes in elemental analysis are due to the blending process itself and not any subsequent aging of LCO EIP in the resulting blend.

Table 2 presents a summary of the blend data from Table 1 for EIP which is normalized to 100% in order to determine an empirical formula. Data for typical average elemental analyses of TIP or sediment is given also.[12] The trend for blend EIP to contain more oxygen is continued in the

TIP and this is reflected in the average empirical formula which contains an additional CH_2 + H_2O compared with typical EIP.

Included in Table 3 are molecular weight data obtained by vapor pressure osmometry. Note that these data are quite consistent with the molecular weight data obtained by size-exclusion chromatography (570 vs 600-900) considering errors inherent in, in particular single point VPO determinations and in size-exclusion data for molecular weights <1000 Da. for molecular shapes which are likely to be quite different from those of the standards used.

Size-Exclusion Chromatography

EIP samples, when dissolved in tetrahydrofuran (THF) and injected onto a size-exclusion column, are usually characterized by a large, broad peak that corresponds to a molecular mass of 600-900 Daltons. This is consistent with other molecular weight data obtained by vapor pressure osmometry and support the existence of these large molecules in the fuels studied.

Also observed are minor amounts of lower molecular mass peaks which probably correspond to a portion of the EIP which dissociates during dissolution in methanol or THF, or to minor amounts of fuel components carried along by the EIP procedure. It is not possible to determine the molecular weight of these minor components since they elute outside the calibration range of the column. Also, the refractive index detector precludes any qualitative identification of these materials.

The large, higher molecular weight peak in the EIP samples is only observed with those fuel or stocks that are subject to oxidative storage instability, i.e., unhydrotreated catalytically cracked LCO's. Some oxidatively stable fuel/stocks such as straight runs will yield small but measureable amounts of EIP solid after extraction. However, this solid, when dissolved in THF and analyzed by SEC does not display the higher molecular weight peak seen in the EIP from cracked stocks. Only a low molecular weight chromatogram is observed which corresponds to the low molecular weight region of the EIP chromatograms from cracked stocks. The largest yield os straight run EIP observed to date is less than 5 mg/100 mL.

Gas Chromatography

GC/MS analysis of the original methanol extract of fuels before EIP precipitation reveals numerous polar species at low concentration. Detailed analysis of these samples revealed several compound types including phenalenes, phenalenones and indoles. Semi-quantitative analysis of these species from six different fuels which spanned a wide range of stabilities failed to reveal any relationship between any combination of these species and the ultimate sludge forming tendencies of the fuels.

When EIP samples are isolated from the methanol extract and then re-dissolved in methanol they may be subjected to analysis by GC. The dissolved EIP gave chromatograms with essentially no peaks eluting in the range of any fuel components including those moieties commonly thought to be precursors to instability. Since there appeared to be a strong link between the original methanol extract and oxidative instability we took this as supportive evidence that it was the solid EIP which contained the precursors to the formation of insoluble sediment and further this EIP itself contained no entrapped fuel. The essential absence of any fuel component peaks in any of the chromatograms led to the conclusion that the methanol fraction contained the presence of higher molecular weight species which were not eluted under the standard experimental GC conditions employed.

This also demonstrates very clearly that the EIP does not contain any entrapped fuel species. This is an important fact in the subsequent interpretation of the PYR/FIMS data.

Pyrolysis/Field Ionization Mass Spectrometry (PYR/FIMS)

Three representative EIP samples were chosen for PYR/FIMS analysis. These were SR-1, LCO-3 and LCO-5. The EIP were isolated as a solid powder and then completely dissolved in toluene in order to introduce a homogeneous sample into the glass capillary for pyrolysis field ionization MS. Most of the toluene was removed by evaporation and then the remaining solid sample of EIP was heated at a controlled rate up to 500° C in the high vacuum source region of the MS. Subsequent weighing of the capillary tube revealed that essentially 100% by weight of the EIP had been pyrolyzed and volatilized by this procedure. Identical analyses of TIP/sludge generally show that less than 60% of the sample is consumed after pyrolysis leaving considerable char in the sample tube.

Representative data for LCO-3 are shown in Table 4. Residual toluene solvent is not shown in the figure but volatilized between approximately 30 and 125° C. Since no other ions up to 300 daltons were seen in this region it can be concluded that the original EIP samples were essentially free of entrapped fuel. In addition, as noted above, GC analysis of EIP which are re-dissolved in methanol reveal no entrapped fuel components.

The total ion mass chromatograms for the pyrolysis FIMS are quite complex. This underscores the tremendous amount of pyrolysis that the EIP samples are undergoing. At the same time it is noteworthy that the entire sample is volatilized/pyrolyzed in a fairly narrow range from 175 to 375° C. The calculated number average molecular weight of the LCO-5 EIP by this process is 582 daltons and the calculated weight average molecular weight is 687. This is in fairly good agreement for the VPO determined molecular weight of this sample (see Table 3).

Due to the complexity of presenting the data in the form of mass pyrograms for subsequent interpretation, an alternative approach has been taken. About half of the total ion current of the mass pyrogram is contained in a number of series of homologous ions separated by 14 dalton increments. These homologous ion series have been arbitrarily assigned a mass identification number, usually one of the lowest mass ions in a particular series. In the case of data for Table 4 only the most intense ion in a particular series was used to generate the temperature profile. In the case of data for Table 5 the sum of all the ions in a particularly identified ion series was determined. The mass intensity values in all cases have been taken from normalized spectra. In addition, the base peaks for all three spectra (in ion counts) were very close in intensity. For this reason the ion counts were not converted to percent relative abundance as is normally done but instead are converted to a normalized ion count.

At this point it is possible to attempt a more detailed analysis of the nature of the EIP sample as revealed by the mass pyrogram in Table 4. The 9 ion series identified account for the 9 most intense sets of masses. Most of the mass peaks in Table 4 are pyrolysis fragments of the high molecular weight EIP. This is supported by the fact that the major series below 300 daltons continue to form over the entire temperature range between 90 and 360° C. As the temperature of the pyrolysis increases the pyrolyzate fragments of higher molecular weight begin to appear (between 300 and 600 daltons) up to temperatures of 400° C.

Even the highest molecular weight fragment ion series probably arise from the pyrolysis of even higher molecular weight material in the EIP. Some less intense series are seen at about 641 daltons and there are even indications of some material as high as 1022 daltons. The lower molecular weight fragment ions probably arise as a combination of pyrolysis of the original very high weight material and pyrolysis of intermediate weight material. As an example of the latter, the series at 131 daltons could arise early in the thermogram as pyrolyzates of the 309 dalton series and later in the thermogram as pyrolyzates of the 563 dalton series.

This is in contrast to the seemingly similar PYR/FIMS results for TIP/sludge or sediment which precipitates out of fuel.[18] This latter material does show a tendency to carry along fuel entrained polars such as indoles and phenalenes. This is not seen in EIP probably because of the way in which EIP is isolated initially. This effect of TIP to include significant amounts of entrained fuel make the interpretation of the PYR/FIMS much more difficult.

The actual interpretation of the identity of the pyrolyzate fragments or of the identity or nature of their parent compounds is clearly beyond the scope of the PYR/FIMS technique. Although it is tempting to equate the lower molecular weight series with such compounds as indoles and phenalenes this is not possible for several reasons discussed below.

First, independent pyrolysis/high resolution mass spectral analysis of the series at 180 has shown that the empirical formula for this ion series is $C_{13}H_{10}N$ (see also Table 5) and this is not consistent with its interpretation as phenalene or phenalenone. Second, although the high resolution mass spectral empirical formula for the pyrolyzate series designated 131 indicate a formula consistent with indoles, other isoelectronic compound types such as divinyl pyridines are equally possible. Although indoles can exist in the fuel at relatively high concentrations, it would be interesting to specifically examine freshly refined fuels for other reactive species such as divinyl pyridines. The major products from model studies[11] of the acid catalyzed reaction of indole with phenalenone have been analyzed by PYR/FIMS and show two major ions at 295 and 410 daltons. If a condensation mechanism is postulated whereby one molecule of indole adds to one molecule of phenalenone with the loss of 2 hydrogens, this would indeed result in an ion at 295 daltons. Similarly a condensation of two molecules of indole with one of phenalenone (with loss of 4 hydrogens) would result in an ion at 410 daltons. Since the ion series at 131 in the EIP samples analyzed is not due to entrapped fuel molecules, but to pyrolysis of higher molecular weight species, if the pyrolyzate fragment is due to indole then the loss of two hydrogens would both come from the phenalenone reactant in the model studies.

This would result in a mass spectral series at 178 which is not observed in EIP PYR/FIMS. However, there is evidence in the model reactions above, that phenalenone is first reduced to phenalenol by the addition of two hydrogens. The phenalenol then reacts with indole (with loss of 2 hydrogens) to give the product at 295 daltons. Upon subsequent pyrolysis the resulting fragments would be at 131 (indole) and 180 daltons (isomerized back to phenalenone). It is unlikely, though, that phenalene or phenalenone is responsible for this series in the EIP PYR/FIMS since the high resolution mass spectral empirical formula for the 180 series contains nitrogen.

Thus, although it is probable that the series at 131 daltons is indoles and that the series at 180 is not phenalenones, it is simply not possible on the basis of PYR/FIMS data alone to determine the actual identity of the original reactants in actual fuel systems.

It has been recently shown by Marshman[13] that in reactive sludge forming fuels neither indoles nor phenalenes in the fuel are the limiting reagents to insolubles sediment. Although much earlier work by Hiley[5-8] and others has demonstrated the participation of these fuel containing species in unstable fuel oxidation, it may be that their actual importance lies in their ability to form highly colored complexes, i.e., this may be the mode of color formation of the liquid fuels. Unfortunately the relationship between color and actual sludge formation rates does not exist as a simple or universal correlation.

Much attention has been given in earlier work to the formation of acidic species in the catalytically cracked LCO stocks which are of sufficient strength and concentration to catalyze condensation reactions leading to higher molecular weight species and thus to TIP/sludge. Again, Marshman[13] was unable to state that acidity of the fuel during the sludge formation process was the limiting factor in the production of insolubles. More recent reports have investigated this possibility and found that reactive LCOs are generally not acidic, whereas non-reactive straight run distillate streams are usually highly acidic.[14] Additional work which has carefully monitored blended fuel acidity formation rates and sludge formation rates has also shown that there is no dependence of sludge formation on acidity.[15-16] It would be of interest in the future to determine whether there is an effect of acidity on EIP formation.

As conjectured in an earlier paper in this series[1], one of the two possible alternative origins of EIP is that a fuel soluble macromolecular species (possibly porphyrinic in nature) is carried over into the fluid catalytic cracker by the feed stock and ends up in the product blending stream. This macromolecular species could then further oxidize (making it more polar and soluble in methanol, at which point it is EIP). Finally further oxidation and condensation reactions with reactive fuel monomers precipitates the final product insoluble sediment or sludge.

Since the above conjecture rests upon a geochemical/processing origin one would then expect that the EIP from various sources would be somewhat similar at least in gross structural features. The PYR/FIMS data for the two LCOs given in Table 5 and Figure 1 strongly indicate that this alternative origin for EIP is probably not correct. Although there are some strong similarities in the three EIP samples such as the mass series at 131 and 309, there exist major dissimilarities. In addition to this, a common geochemical origin for EIP would be porphyrinic in nature and the PYR/FIMS fragments of such an EIP moiety would result in significant amounts of pyrrolic species evolved below 300 daltons and these do not occur.

The traditional explanation for the origin of TIP/sludge or sediment postulates reactive monomeric fuel components which oxidize and condense to form larger and more polar and less fuel soluble species. The fact that the EIP species must themselves further oxidize and condense to form TIP/sludge means that we now have a probe of some intermediate stage in sludge formation from reactive fuel monomers which is itself a simpler species compositionally and is much more amenable to analysis. In fact, the EIP themselves are simply produced by reactive fuel monomeric species. This last statement suggests that the detailed chemical nature of the EIP and the sediment itself must be quite fuel dependent and the data in Table 5 and Figure 1 support this very clearly.

This information together with the fact that the PYR/FIMS data clearly support the elemental analysis data of the EIP which implicates nitrogen and oxygen containing compounds underscores the need to continue to determine the precursors of EIP in the original fuel. The fact that EIP are formed from reactive fuel monomers implies that freshly refined LCO's will not initially have EIP present and this is the subject of our current investigations. If an LCO or LCO blend has formed as little as 20 mg/L of EIP, then the LCO itself is probably of little use in studies designed to determine the compositional precursors of either EIP or TIP/sludge. It is for this reason that many very carefully performed studies to date have not been able to pinpoint the real precursors of sludge formation. Certainly if an LCO contains high total nitrogen or indoles content it also contains the real precursors to sludge. These indicators, however, are not able to be directly or quantitatively linked to any given fuel's sludge forming tendency.

Conclusions

All of the EIP samples analyzed for this work were from fuels which had already developed EIP, i.e., they were at least 6 months old since production. Molecular weights from SEC, VPO and PYR/FIMS were all consistent in the range of 650 to 1000 daltons. The EIP have proven to be considerably easier to analyze than the actual sludge which they apparently produce ultimately.

Since it has been shown that the EIP do not arise as a geochemical/processing artifact it can be concluded that they arise from the oxidation and condensation of reactive fuel monomers. Clues as to the nature of these fuel species are found in the elemental analysis and empirical formulas for EIP which indicates much involvement of oxygen and nitrogen. Further information from the high resolution mass spectral empirical formulas and from the PYR/FIMS indicates that nitrogen containing precursors in the fuel with a formula of $C_nH_{2n-9}N$ and C_nH_{2n-15} are involved in the generation of EIP. The 2n-9 class includes such isoelectronic possibilities as indoles, divinyl pyridines and dihydroquinolines. The 2n-15 class includes such isoelectronic possibilities as benzoindoles, phenalidines, divinyl quinolines, carbazoles, acridines and phenanthridines.

The EIP are more amenable to PYR/FIMS analysis as evidenced by their complete pyrolysis than the more highly oxidized and polar TIP/sludge. Even so, the PYR/FIMS technique subjects the EIP to a tremendous amount of pyrolysis. Because of this the interpretation of pyrolyzate ions to reconstruct the formation of EIP is not possible.

Only freshly refined, unhydrotreated, catalytically cracked LCO material will be suitable for future studies involving the determination of the fuel precursors of EIP and whether the formation of EIP can be inhibited by antioxidant additives. Essentially no work on the determination of fuel precursors to sludge to date has appreciated the importance of this fact. Certainly no work presented to date has verified the initial absence of EIP before beginning a detailed compositional analysis and this is essential. By the time a measurable amount of EIP has formed, it is quite possible that all of the actual precursors to sludge are already well on their way to the dimer/trimer stage and hence no longer amenable to simple GC analysis techniques to monitor their depletion from the fuel.

References

(1) Hardy, D.R. and Wechter, M.A. *Energy & Fuels*, **1990**, 4, 270.

(2) Wechter, M.A. and Hardy, D.R. *Fuel Sci. and Tech. Int.* **1989**, *7*(4), 423.

(3) Wechter, M.A. and Hardy, D.R. *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Giles, H.N;(Ed.) CONF-911102; U.S. Department of Energy: Washington, D.C. **1992**; 620.

(4) Chertkov, Y.B.; Likhterova, N.M.; and Gorenkov, A.F. *Khimiya i Tekhnologiya Topliv i Masel*, **1989**, *8*, 26.

(5) Pedley, J.F.; Hiley, R.W. and Hancock, R.A. *Fuel* **1987**, *66*, 1646.

(6) Hiley, R.W.; Pedley, J.F. *Fuel* **1988**, *67*, 469.

(7) Pedley, J.F.; Hiley, R.W. and Hancock, R.A. *Fuel* **1988**, *67*, 1124.

(8) Pedley, J.F.; Hiley, R.W.; Hancock, R.A. *Fuel* **1989**, *68*, 27.

(9) Bhan, O.K.; Brinkman, D.W.; Green, J.W. and Carley, B. *Fuel* **1987**, *66*, 1200.

(10) Malhotra, R. and Hazlett, R.N., *Prepr.- Am. Chem. Soc., Div. Fuel Chem.* **1990**, *35*, 1163.

(11) Malhotra, R.and Hazlett, R.N. *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*; Giles, H.N.(Ed.); U.S. Department of Energy: Washington, DC, **1992**, 518.

(12) Beal, E.J.; Cooney, J.V.; Hazlett, R.N.; Morris, R.E.; Mushrush, G.W.; Beaver, B.D. and Hardy, D.R. "Mechanisms of Syncrude/Synfuel Degradation," Naval Research Laboratory Final Report DOE/BC/10525-16, **1987**.

(13) Marshman, S.J.; " *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*" Giles, H.N.(Ed.), U.S. Department of Energy, Washington, D.C. **1992**, 489.

(14) Green, J.B.; Stirling, K.Q. and Ripley, D.L. *Chemical Causes of Light Cycle Oil Storage Instability*, Report NIPER-6857-F, NIPER, Bartlesville, OK, **1991**.

(15) Wechter, M.A. and Hardy, D.R. *Energy & Fuel* **1989**, *3*, 461.

(16) Hardy, D.R. and Wechter, M.A. *Fuel* **1990**, *69*, 720.

(17) Hazlett, R. N., *Fuel Sci. Technol. Int.* **1988**, *6*, 185.

(18) Hazlett, R. N.; Hardy, D. R. and Malhotra R.; *Energy & Fuels*, submitted 1993.

Table 1. Elemental Analysis of Selected EIP. Direct determination of CHON.

Fuel Code	Fuel Type	% C	% H	% O	% N	% Total
SR-1	100% SR	76.7	7.2	7.8	4.5	96.2
LCO-2	100% LCO	79.4	6.1	9.9	2.5	97.9
LCO-3	100% LCO	83.2	6.5	4.6	4.8	99.1
LCO-5	100% LCO	84.2	6.7	3.1	5.6	99.6
B-2	20% LCO	75.3	6.1	10.1	4.9	96.4
B-5	20% LCO	79.4	6.3	7.5	3.0	96.2
B-5*	20% LCO	75.2	6.4	9.8	5.5	96.9
B-13	20% LCO	76.5	6.4	9.1	4.9	96.9
B-14	20% LCO	76.5	5.8	10.4	3.3	96.0

*EIP determined after ASTM D5304 stress test.

Fuel Code is: SR = straight run distillate stream
LCO = catalytically cracked light cycle oil
B = blend of 20% LCO + 80% SR v/v

Table 2. Elemental Analysis Averages (normalized to 100%) for a wide range of 20% LCO blends for EIP and Sediment. Empirical formula also computed from these data.

Property	EIP	Sediment/TIP
% Carbon	79.4	75.4
% Hydrogen	6.4	6.9
% Oxygen	9.7	13.7
% Nitrogen	4.5	4.0
Empirical Formula	$C_{21}H_{20}O_2N$	$C_{22}H_{24}O_3N$

Table 3. Molecular Weight Analysis by Vapor Pressure Osmometry (VPO) for selected EIP samples (in Daltons).

Fuel Code	Single Point	Triple Point
SR-1	645	Not determined
LCO-3	513	525
LCO-5	486	679

Table 4. EIP of LCO-3 analyzed by pyrolysis FIMS. Mass ID referred to the major mass in that homologous mass series from the pyrolyzate. As the temperature of the sample is raised from 100 to 400 C the major ion intensities (raw data counts) are summed for that temperature range. (-) indicates a value close to zero ion counts.

Mass ID	Probe/Sample Temperature Range °C						
	90-150	164-201	203-250	254-299	303-355	359-399	SUM
131	1.2	2.8	4.5	2.2	0.6	0.1	11.4
180	4.0	6.5	1.0	-	-	-	11.5
181	1.5	1.1	1.0	0.6	0.3	-	4.5
202	0.7	1.2	0.3	-	-	-	2.2
309	0.3	0.9	3.7	1.5	0.4	-	6.8
438	-	0.4	5.2	6.1	1.5	0.1	13.3
563	-	-	0.7	9.7	12.5	2.1	25.0
580	-	-	3.5	4.2	0.5	0.5	8.9
581	-	-	2.2	3.4	1.0	0.7	7.3
SUM-->	7.7	12.9	22.1	27.7	16.8	3.5	90.9

Table 5. Pyrolysis FIMS comparative analysis of several EIP solids. The major homologous series are identified by a mass which is generally the highest in the series, but not always. Compare these values for the sum of the homologous series for the entire pyrolysis temperature range to the totals for an individual mass given in Table 4. Compound type empirical formulas for the ion series given is from independent high resolution exact mass (to 10^{-4} mass units) data.

Mass Series ID	Empirical Formula	LCO-3	LCO-5	SR-1
131	C_9H_9N	34	21	46
156	---	0	20	3
180	$C_{13}H_{10}N$	28	51	0
181	$C_{13}H_{11}N$	14	57	3
202	---	5	24	0
261	---	0	0	51
309	$C_{22}H_{15}NO$	19	35	16
438	$C_{31}H_{22}N_2O$	41	54	27
563	---	78	9	0
580	---	25	0	0
581	---	23	0	0

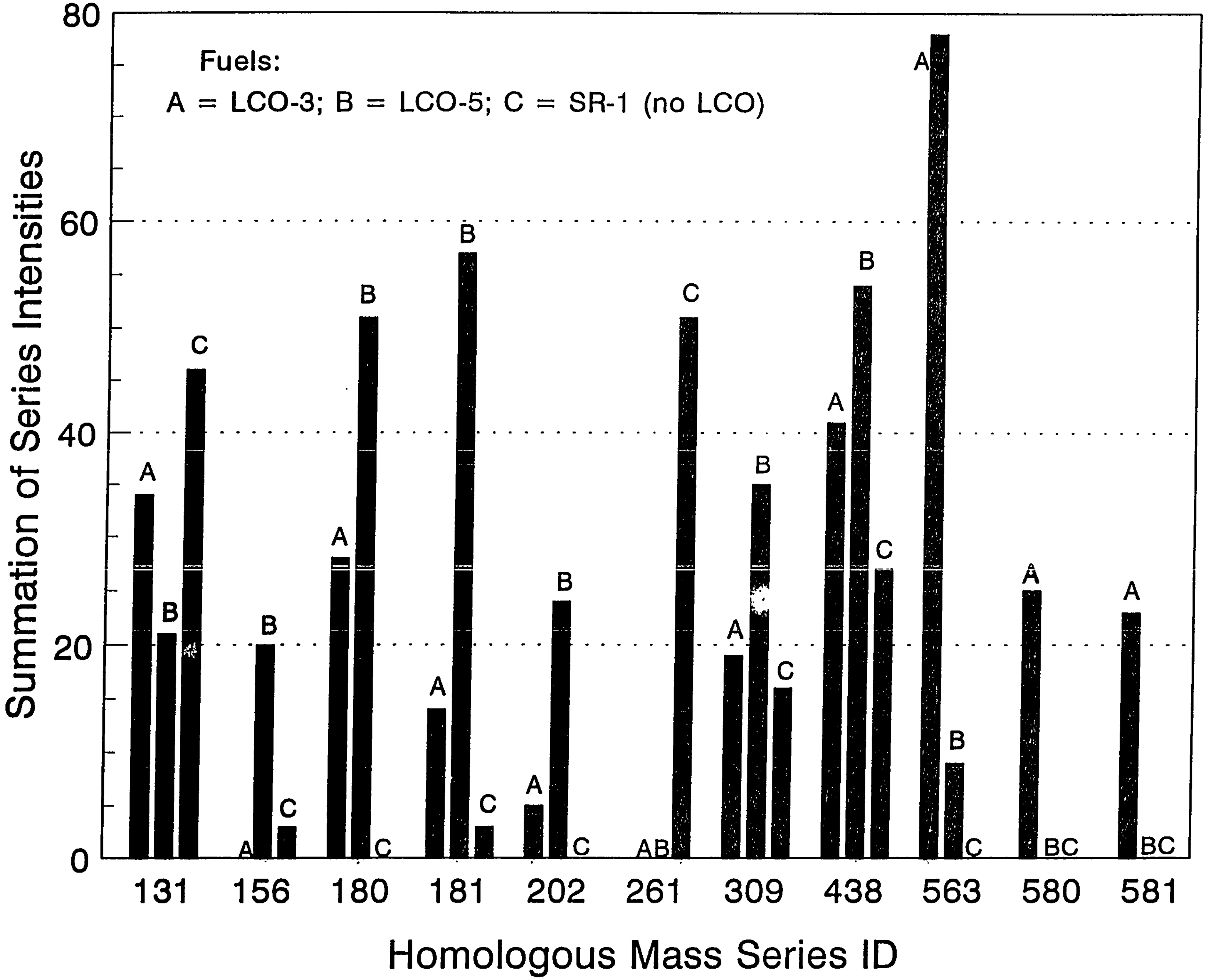

Figure 1. PYR/FIMS data for the EIP from three fuels. A = LCO-3, B = LCO-5, C = SR-1 (no LCO). See text for details regarding the mass series ID.

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THE EFFECT OF INCREASED REFINING ON THE LUBRICITY OF DIESEL FUEL

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ABSTRACT

The United States and Europe are mandating increasingly severe diesel fuel specifications, particularly with respect to sulfur content, and in some areas, aromatics content. This trend is directed towards reducing vehicle exhaust emissions and is generally beneficial to fuel quality, ignition ratings, and stability. However, laboratory studies, as well as recent field experience in Sweden and the United States, indicate a possible reduction in the ability of fuels to lubricate sliding components within the fuel injection system. These factors, combined with the trend toward increasing injection pressure in modern engine design, are likely to result in reduced durability and failure of the equipment to meet long-term emissions compliance. The Belvoir Fuels and Lubricants Research Facility (BFLRF) developed an accelerated wear test that predicts the effects of fuel lubricity on injection system durability. This test now has been widely used by fuel, additive, and equipment manufacturers. Several thousand fuel samples have been evaluated to date, and collectively, they form one of the largest data bases on fuel lubricity currently in existence. This range of data permits a good overview of the commercially available fuels and confirms a general decrease in fuel lubricity due to increasing refining severity. The results indicate that no high-sulfur fuel (>0.12 wt%) had poor lubricity, while a number of low-sulfur fuels (<0.05 wt%) did produce unacceptable wear. The lubricity of many severely refined fuels is probably being restored using relatively high concentrations of additive.

INTRODUCTION

In the United States, visible smoke from heavy-duty diesel engines has been subject to regulation by the Environmental Protection Agency (EPA) since 1970. Increasingly severe regulations for hydrocarbon (HC), oxides of nitrogen (NO_x), and particulate matter (PM) emissions were implemented throughout the 1980s and into the 1990s. Initially, these requirements were achieved through improvements in the combustion system (comprised of the combustion chamber, injection equipment, ignition timing, etc.). However, the increasingly stringent particulate requirements implemented in the 1990s require modifications to the composition of the fuel as well as the engine hardware to obtain further reductions of emissions.

Diesel fuel specifications have intentionally remained broad to permit the maximum availability and lowest price possible.[1] Historically, many developed nations have allowed a fairly high sulfur content in the range of 0.5 percent by weight (wt%), with no specification on aromatics content.[2] The major industrialized nations are currently tightening diesel fuel quality specifications, with elimination of sulfur the primary concern. Reduction in sulfur content will minimize formation of H_2SO_4 in the atmosphere and will facilitate future development of platinum-catalyzed particulate traps.[1] Data generated in a cooperative study sponsored by the Coordinating Research Council (CRC) as part of their Vehicle Emissions Program (VE 1) confirmed the primary importance of sulfur.[3,4] However, the VE 1 study indicated that exhaust hydrocarbons, carbon monoxide, oxides of nitrogen, and particulate matter were also marginally reduced by decreasing aromatics content. Later studies have indicated that cetane number may be more directly related to emissions than aromatics concentration alone.[5,6]

A selection of the relevant fuel specifications from around the world is summarized in TABLE 1. In 1991 and 1992, Sweden defined several new classes of fuel that regulate a number of fuel characteristics, including sulfur and aromatics content. Different tax classes were designed to provide economic incentives to use the clean burn Class I and II fuels rather than the higher sulfur Class III fuel. Similarly, in the United States, federal regulations implemented by the EPA limited the maximum fuel sulfur content to 0.05 wt% from its previous level of 0.5 wt%, effective October 1993. Based on the VE 1 study, the California Air Resources Board (CARB) mandated an additional requirement of 10 vol% aromatics in diesel fuel sold in California. Alternatively, refiners could certify diesel fuel formulations with equivalent or lower emissions when compared to a CARB-specified, 10 vol% aromatics reference fuel. Lowering the aromatics content of diesel fuels from the previous levels of well over 30 vol% to the 5 or 10 vol% mandated by the newer regulations requires severe hydrotreatment (i.e., reaction of intermediate petroleum products with hydrogen) for many refineries. As a result, some California fuel producers are minimizing the level of refinery processing by developing alternate fuels that will demonstrate equivalent emissions and will have slightly higher aromatics content.[7]

Many components within the fuel injection system rely on fuel for effective lubrication and wear resistance. Hydrotreating reduces trace components, such as oxygen- and nitrogen-containing compounds, as well as polycyclic aromatics. The chemically active and polar compounds, necessary only to provide additive solubility in formulated oils, are the only active components present in fuels to minimize wear. The lubricating characteristics of crankcase oils are significantly altered by hydroprocessing during production of the basestock, as opposed to conventional solvent refining. In particular, lubricant oxidation stability is increased, but inferior additive solvent characteristics are apparent.[8] It is fair to assume that this type of hydrotreatment will affect fuel-lubricating qualities.

A U.S. Army-sponsored study indicated that full-scale fuel injection systems commonly contained adhesive wear,[9-12] which is not accurately measured in fuel lubricated contacts by any existing wear test.[13] As a result, a test procedure that uses the Ball-on-Cylinder Lubricity Evaluator (BOCLE) was developed. This procedure is commonly referred to as the U.S. Army Scuffing Load Wear Test.[14,15] Previously published results based on this test using a small number of fuels indicated a directional correlation between fuel lubricity and refining severity.[14] Since that time, several thousand fuels and additives have been evaluated for military and commercial sponsors using this test. The resulting data base is likely to be one of the largest currently in existence, and it provides an improved insight as to the effects of refining severity on fuel lubricity.

EXPERIMENTAL

The U.S. Army Scuffing Load Wear Test[14,15] determines the minimum applied load (MAL) required for a step transition to adhesive scuffing. Thus, MAL is related inversely to wear. Recently, it has been incorporated into Federal Specification VV-F-800E for diesel fuels[16] and is now used as an interim measurement of fuel lubricity by a number of fuel and engine manufacturers. In addition, the test has been recommended as an interim minimum lubricity requirement for the state of California, pending acceptance of a final standard.[17] The U.S. Army Scuffing Load Wear Test shows good correlation with a wide range of full-scale equipment types. A minimum scuffing load capacity of approximately 2,800 grams MAL is necessary to provide acceptable equipment durability. However, a number of organizations have adopted slightly different minimum fuel lubricity requirements, based on the application and the margin of safety desired.

To date, several thousand fuels have been evaluated using the U.S. Army Scuffing Load Wear Test. Permission was obtained from a majority of the original sponsors to include anonymous data in the present study, resulting in a data base of approximately 1,000 fuels. The complete data base includes experimental and pilot fuels, and those fuels believed to meet EPA and CARB requirements. A number of high-sulfur fuels (<0.5 wt%) are also included as a baseline for comparison. Each of the participating sponsors was requested to provide as much information as possible relating to each fuel. Nonetheless, complete analysis was not available for many of the fuels, reducing the number of data points in some plots. Where possible, ASTM procedures D 4294, 5186, and 445 were used to generate sulfur, aromatic, and viscosity data, respectively. However, the data were obtained from a number of sources, and so may contain reproducibility errors between laboratories. All data pertaining to polyaromatics content were generated at the authors' laboratory using a modified version of ASTM D 5186.

The data base may be conveniently subdivided into the following categories, which are discussed throughout the remainder of the text and also defined in TABLE 2:

a) The category referred to as "High-Sulfur" contains fuels which are similar to those historically sold throughout the United States prior to implementation of the 1993 regulations. Only fuels with a sulfur content greater than 0.12 wt% were considered to be high in sulfur. Fuels in this category probably do not contain lubricity additives and are used as a baseline for comparison with the newer fuels defined below.

b) The "EPA Fuels" category consists of commercially available, low-sulfur fuel samples believed to meet EPA regulations. They have a sulfur content below 0.05 wt% and were obtained throughout the United States (excluding California) following implementation of the 1993 regulations. Some of these fuels may contain lubricity additives.

c) The "CARB Fuels" category consists of commercially available, low-sulfur fuel samples believed to meet CARB regulations. They have a sulfur content below 0.05 wt% and were obtained from California following implementation of the 1993 regulations. These fuels must meet the additional requirement mandated by CARB of 10 vol% aromatics or equivalent emissions. Most of these fuels are believed to contain lubricity additives.

d) The largest category represents the complete data base and contains many fuels of unknown origin and additive content.

It should be noted that the average sulfur content of both the EPA and CARB fuel categories is appreciably below the maximum of 0.05 wt% specified by the EPA. Indeed, approximately one-quarter of the CARB fuels sampled had a sulfur content below 0.01 wt%.

RESULTS

Effect of 1993 Federal and State Fuel Specifications: Graphs summarizing the test results obtained using the U.S. Army Scuffing Load Wear Test are shown in Fig. 1. Four separate histograms show the data distribution of results (i.e., each bar represents the number of samples which produce a given result) for each of the data categories described in TABLE 2. The topmost histogram is from the complete data base. The distribution of results is between 1,000 and 5,000 grams MAL, with a mean of approximately 3,000 grams. However, these data are not necessarily representative of commercially available samples.

The remaining three histograms in Fig. 1 show results for high-sulfur, CARB, and EPA fuels. As expected, none of the high-sulfur fuels produced a scuffing load capacity below 2,800 grams, which is believed to be the minimum result necessary to provide long-term equipment durability. By comparison, a relatively large number of both the CARB and EPA fuels produced results that fall below the 2,800-gram durability minimum. Furthermore, several fuels produced results below 2,000 grams, which corresponds to very poor lubricity. The tests for several of the lower lubricity fuels were obtained (but not plotted) in duplicate to minimize the possibility of error with these more critical fuels.

Significantly, three of the lowest lubricity fuels, as measured using the U.S. Army Scuffing Load Wear Test, were reported to have reduced equipment durability at three separate military bases. The results for these fuels are highlighted in black in Fig. 1. The fuel injection system failure rates recorded at one of the three bases are summarized in Fig. 2 on a month-by-month basis (detailed data are not available from the other bases). Failure rates approximately doubled following September 1993, which corresponds to the introduction of the low-sulfur fuel, highlighted in gray. Indeed, the Army base reported that a number of replacement pumps have failed for the second time. The failure rate was marginally reduced in June 1994 by the addition of 250 mg/L of a dilinoleic, acid-based lubricity additive that increased the scuffing load capacity to 3,000 grams from its original level of 1,600 grams. However, the additive was only added sporadically during the following months due to procurement problems, which may reduce the benefits observed.

General Effects of Refining Severity on Fuel Lubricity: It is unlikely that a perfect correlation between chemical composition and lubricity will be easily derived, considering the multitude of surface-active compounds present in each fuel. In addition, many compounds affect lubricity at concentrations as low as 20 parts per million (ppm). Nonetheless, a broad correlation between lubricity and refining severity, as indicated by sulfur or aromatics content, would be useful. Increasingly severe hydrotreatment will initially reduce sulfur compounds, followed by the higher molecular weight aromatics. The correlation between fuel sulfur content and scuffing load capacity is shown in Fig. 3. This figure includes the complete fuels data base, including additized and experimental fuels. Although no direct correlation exists between sulfur content and fuel lubricity, no fuel with a sulfur content above 0.12 wt% showed poor lubricity. Many unadditized low-sulfur fuels showed good lubricity as well. As a result, it is impossible to differentiate among post-1993, low-sulfur fuels on this basis alone.

The correlation between total aromatics content and scuffing load capacity is shown in Fig. 4a. Some directional correlation exists, although very high total aromatics content is necessary to ensure good lubricity. Significantly, however, fuels with an aromatics content below 10 wt% that did not contain a lubricity additive did not have good lubricity. The correlation between fuel lubricity and diaromatic content is shown in Fig. 4b, while Fig. 4c illustrates the correlation between fuel lubricity and polyaromatic content. In both instances, a significantly improved correlation is present compared with the correlation for total aromatics content. As expected, low-aromatic fuels that contain additives typically show unexpectedly good lubricity. However, the additives appear to have little effect on better lubricity fuels.

Scuffing load wear tests were performed to define the effect of 26 compounds on lubricity. Mono- and diaromatic compounds were added at 5 wt%, and polyaromatic and olefin compounds were added at 1 wt%. Organosulfur compounds were added at 0.5 wt% sulfur content concentration to reflect their normally lower concentration in real fuels. Most of the compounds produced a marginal increase in the scuffing load capacity of the fuel, normally becoming more effective as molecular weight increased. However, none of the compounds increased scuffing load capacity to the extent predicted by consideration of sulfur and aromatic content in real fuels, as shown in Figs. 3 and 4. It is likely that sulfur and aromatics compounds simply reflect the effects of refinery severity on other surface-active compounds in the fuel.

Effect of Lubricity Additives: A wide range of both commercially available and experimental lubricity additives have been evaluated using the U.S. Army Scuffing Load procedure. In general, the response obtained from lubricity additives depends on both additive concentration and the lubricity of the base fuel. The combined effects of both variables were plotted using a wear mapping procedure similar to that developed in Reference 9. The increase in scuffing load capacity produced by lubricity additives is plotted in Fig. 5 as a simultaneous function of additive concentration and the scuffing load capacity of the fuel without additive. (The increase in scuffing load capacity is defined as the result obtained for the additive-containing fuel minus the result obtained for the neat fuel.)

Fig. 5 was generated from approximately 400 fuel and additive combinations. Most of the additives used are commercially available, although some experimental compounds are also present. Ineffective additives were excluded from the data base, so the curve represents the results obtained for the better additives averaged over a number of neighboring data points. The step transitions on the surface are the result of the smoothing process. Clearly, Fig. 5 only reflects the broad trends observed and does not imply that all additives fit this description. However, most additives produced surprisingly similar results, and in general, additive effectiveness increases with concentration up to approximately 100 to 200 mg/L. Further increases in concentration up to approximately 400 mg/L only marginally increase wear resistance. Additive concentrations of 1,000 and 2,000 mg/L are widely used, but typically provide no additional protection. These higher concentrations are normally found with multifunctional additive packages, which contain a number of additives dissolved in a carrier fluid to facilitate blending at the vehicle.

The additive concentration required to increase the scuffing load capacity of the fuel is considerably greater than that needed to eliminate the oxidative corrosion wear mechanism which predominates in jet kerosene fuels.[13] Additive concentrations specified in MIL-I-25017 for military aviation fuels typically range from 9 to 22.5 mg/L.[18] Such concentrations successfully eliminate surface oxidation without providing a strong boundary layer and show little or no improvement in scuffing wear resistance. The composition of most additives evaluated in the present study is unknown. Significantly, however, the increase in scuffing load capacity plotted in Fig. 5 is typical of that observed for high concentrations of simple dimer acid compounds normally used as corrosion inhibitors in additives qualified under MIL-I-25017.

The benefits provided by the lubricity additives are also sensitive to fuel composition, with the poorest lubricity fuels experiencing the greatest improvement. In general, the optimum additive concentration increased the scuffing load capacity of the fuel to approximately 3,500 grams, irrespective of the initial lubricity of the base fuel. This corresponds to the lubricity of a good, high-sulfur fuel and may normally be achieved using a high concentration of a dimer acid.

However, a number of exceptions were observed in which the effectiveness of a single additive was found to vary greatly between two fuels of similar initial lubricity.

Alternate Fuel Blends: A number of alternate solutions for low lubricity beside traditional lubricity additives have been evaluated at our laboratory. In many instances, blending a small volume of good lubricity fuel provides a significant improvement in wear resistance to a low lubricity fluid. For many fuel streams, the level of hydrotreatment necessary to reduce aromatics content below 10 to 15 percent virtually eliminates sulfur from the final product. As a result, some back-blending of a high-sulfur feedstock with the final product may occur without exceeding the 0.05 wt% sulfur limit and with only a marginal effect on aromatics content.

The effects of blending three different high-sulfur diesel fuels with neat Jet A-1 kerosene fuel are shown in Fig. 6. Fuel A is particularly effective, and the lubricity of the Jet A-1 fuel is improved by approximately 1,200 grams when the combined sulfur content of the blend is 0.05 wt%. It should be noted that the Jet A-1 base fuel is of especially low lubricity and initially contains only 0.002 wt% sulfur. This increase would be sufficient to improve the lubricity of all the fuels in Fig. 1 to the 2,800-gram minimum lubricity level. However, fuels B and C are less effective in improving lubricity at similar total sulfur concentrations. Conversely, kerosene fuels are commonly blended with higher viscosity fuels to allow their use in arctic conditions. In this instance, dilution with kerosene fuel will produce a marked decrease in overall lubricity.

Alternative fuels, such as biodiesel, serve as both a BTU source and as a low emission component for exhaust emissions control. In the United States, fuels derived from soybean oils are normally blended into diesel fuels at a concentration of 20 percent. The effects of biodiesel on the lubricity of an EPA fuel and a CARB fuel are plotted in Fig. 7. The biodiesel fuel consisted of soybean oil transesterified with methanol to form methyl ester and had exceptional lubricity. The scuffing load capacity of neat biodiesel was in excess of 6,000 grams, which is superior to any diesel fuel evaluated to date. Both the EPA and CARB base fuels had good initial lubricity, which was further improved through blending with biodiesel.

DISCUSSION

The predominant source of lubricity in diesel fuels is minority constituents, which are most likely to interact with fuel-wetted surfaces. These constituents are the more polar molecules that contain heteroatoms and tertiary carbon atoms. It is precisely these molecules that react first when diesel stocks are hydrogenated to improve emissions performance. The identities of the minor constituents are not known but should vary as sulfur and aromatics concentrations are reduced. As a result, it is likely that sulfur and aromatics content simply reflect the level of refining severity present, rather than being a direct measure of lubricity.

The present paper describes a data base obtained using a previously validated, laboratory-scale wear test procedure. The data base includes over 1,200 commercially available and experimental fuels and fuel additive combinations. As expected, all high-sulfur fuels evaluated were at or above the minimum lubricity requirement indicated by correlation with full-scale equipment in previous studies. However, many of the fuels barely exceeded the 2,800-gram minimum. Therefore, it may be assumed that empirical manufacturing experience has optimized the design criteria necessary to provide acceptable durability and performance while operating with these fuel types. As a result, any significant variations in fuel composition, such as a switch to arctic fuel or jet kerosene, have historically required a metallurgical or design modification.

The results contained in the data base confirm that fuel lubricity is directionally correlated to aromatic and sulfur content, resulting in a general decrease in lubricity as more stringent emissions regulations are introduced. In some instances, this change in fuel composition is sufficient to reduce lubricity below the level recommended by the manufacturers for acceptable durability. Indeed, a few low lubricity fuels, similar to those which originally caused durability problems in Sweden, are commercially available in the United States.* However, the potentially widespread use of these fuels precludes retrofitting vehicle fuel injection systems with improved wear resistant metallurgies.

Fortunately, widespread catastrophic failures are not yet being observed in the United States. In contrast to Sweden, the average lubricity of the current United States fuel supply is relatively high, with an average scuffing load capacity of approximately 3,200 grams. It is likely that inadvertent mixing of good and poor lubricity fuels occurs in most commercial applications, resulting in a relatively good lubricity blend. Larger consumers, such as military bases (which depend on a single fuel source), are more vulnerable to the effects of the isolated, low lubricity fuels on the market. As a result, such users are occasionally experiencing decreased durability from the introduction of low-sulfur, low-aromatic fuels.

* Early samples of very low sulfur Swedish fuel that did not contain lubricity additives produced a scuffing load capacity of 1,200 and 1,400 grams for the Class I and II grades, respectively. Later samples that contained lubricity additives produced a scuffing load wear test result in excess of 3,000 grams and did not cause durability problems.

CONCLUSIONS

a) Very low lubricity was observed for a number of commercially available fuels meeting 1993 regulations (i.e., <0.05 wt% sulfur). A number of the lowest lubricity fuels were independently reported to have reduced the durability of the fuel injection system on military vehicles. No data is available for the remaining fuels.

b) All high-sulfur fuels (>0.12 wt%) had good lubricity.

c) Many low-sulfur fuels (<0.5 wt%) had good lubricity.

d) No unadditized fuel with a total aromatics content below 10 percent showed good lubricity.

e) Many post-1993 fuels contained appreciably less than the 0.05 wt% sulfur mandated by the EPA. California fuels were particularly low.

f) The aromatics content of most California fuels was above 10 percent, although the average value remained appreciably below that observed for the remainder of the country.

g) Lubricity additives are effective in improving scuffing load capacity at concentrations above 75 to 100 mg/L and have the most effect in low lubricity fuels.

h) Good directional correlation was observed between fuel lubricity and diaromatic and polyaromatic concentrations.

i) The effects of most lubricity additives evaluated are similar to those produced by dimer acid compounds, such as dilinoleic acid.

j) Poor lubricity fuels may be improved through blending with a small amount of better lubricity fuel, although the effects appear fuel composition-sensitive. Conversely, blending of low lubricity kerosene fuels, as is common in arctic conditions, will reduce the lubricity of the base fuel.

k) Biodiesel fuels consisting of methyl esters have excellent scuffing and adhesive wear resistance that exceed those of the best conventional diesel fuels.

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REFERENCES

(1) Springer, K.J., "Low Emission Diesel Fuel for 1991-1994," *Advances in Engines Emissions Control Technology ICE*, **5**, ASME, 1989.

(2) ASTM Designation: D 975-81, "Standard Specification for Diesel Fuel Oils," ASTM, 1916 Race Street, Philadelphia, PA, 1981.

(3) Ullman, T.L., "Investigation of the Effects of Fuel Composition and Injection Combustion System Type on Heavy-Duty Diesel Exhaust Emissions," Southwest Research Institute Report Prepared for the Coordinating Research Council, Inc., March 1989.

(4) Ullman, T.L., "Investigation of the Effects of Fuel Composition on Heavy-Duty Diesel Engine Emissions," SAE Technical Paper No. 892072, September 1989.

(5) Ullman, T.L., Mason, R.L., and Montalvo, D.A., "Study of Fuel Cetane Number and Aromatic Content Effects on Regulated Emissions from a Heavy-Duty Diesel Engine," Southwest Research Institute Report Prepared for the Coordinating Research Council, Inc., September 1990.

(6) Ullman, T.L., Mason, R.L., and Montalvo, D.A., "Effects of Fuel Aromatics, Cetane Number, and Cetane Improver on Emissions From a 1991 Prototype Heavy-Duty Diesel Engine," SAE Technical Paper No. 902171, October 22-25, 1990.

(7) Nikanjam, M., "Development of the First CARB-Certified California Alternative Diesel Fuel," SAE Technical Paper No. 930728, Presented at SAE International Congress and Exposition, Detroit, MI, March 1-5, 1993.

(8) Galiano-Roth, A.S. and Page, N.M., "Effect of Hydroprocessing on Lubricant Base Stock Composition and Product Performance," *Lubrication Engineering*, **50**, No. 8, pp. 659-654.

(9) Lacey, P.I., "Wear With Low Lubricity Fuels, Part I: Development of a Wear Mapping Technique," *Wear*, **160**, 1993; pp. 325-332.

(10) Lacey, P.I., "Wear With Low Lubricity Fuels, Part II: Correlation Between Wear Maps and Pump Components," *Wear*, **160**, 1993; pp. 333-343.

(11) Lacey, P.I. and Lestz, S.J., "Effect of Low Lubricity Fuels on Diesel Injection Pumps, Part I: Field Performance," SAE Technical Paper No. 920823, Presented at SAE International Congress and Exposition, Detroit, MI, February 24-28, 1992.

(12) Lacey, P.I. and Lestz, S.J., "Effect of Low Lubricity Fuels on Diesel Injection Pumps, Part II: Laboratory Evaluation," SAE Technical Paper No. 920824, Presented at SAE International Congress and Exposition, Detroit, MI, February 24-28, 1992.

(13) Lacey, P.I., "Evaluation of Oxidative Corrosion in Diesel Fuel Lubricated Contacts," *Tribology Transactions*, **37**, No. 2, 1994; pp. 253-260.

(14) Lacey, P.I., "Development of a Lubricity Test Based on the Transition From Boundary Lubrication to Severe Adhesive Wear in Fuels," STLE Preprint No. 94-AM-5J-1, Presented at the 49th Annual Meeting of the STLE, Pittsburgh, PA, May 1-5, 1994.

(15) Lacey, P.I., "Draft Test Procedure for the U.S. Army Scuffing Load Wear Test," Available from Belvoir Fuels and Lubricants Research Facility, Southwest Research Institute, P.O. Drawer 28510, San Antonio, TX 78228-0510.

(16) Federal Specification for Fuel Oil, Diesel, VV-F-800E, Revised July 13, 1994, Available from Std. Document Order Desk, Bldg. 4D, 700 Robbins Ave., Philadelphia, PA 19111-5094.

(17) Report of the Diesel Fuel Task Force, Presented to the Honorable Pete Wilson, Governor of California, February 18, 1994.

(18) Military Specification MIL-I-25017E, "Inhibitor Corrosion/Lubricity Improver, Fuel Soluble (Metric)," 15 June 1989.

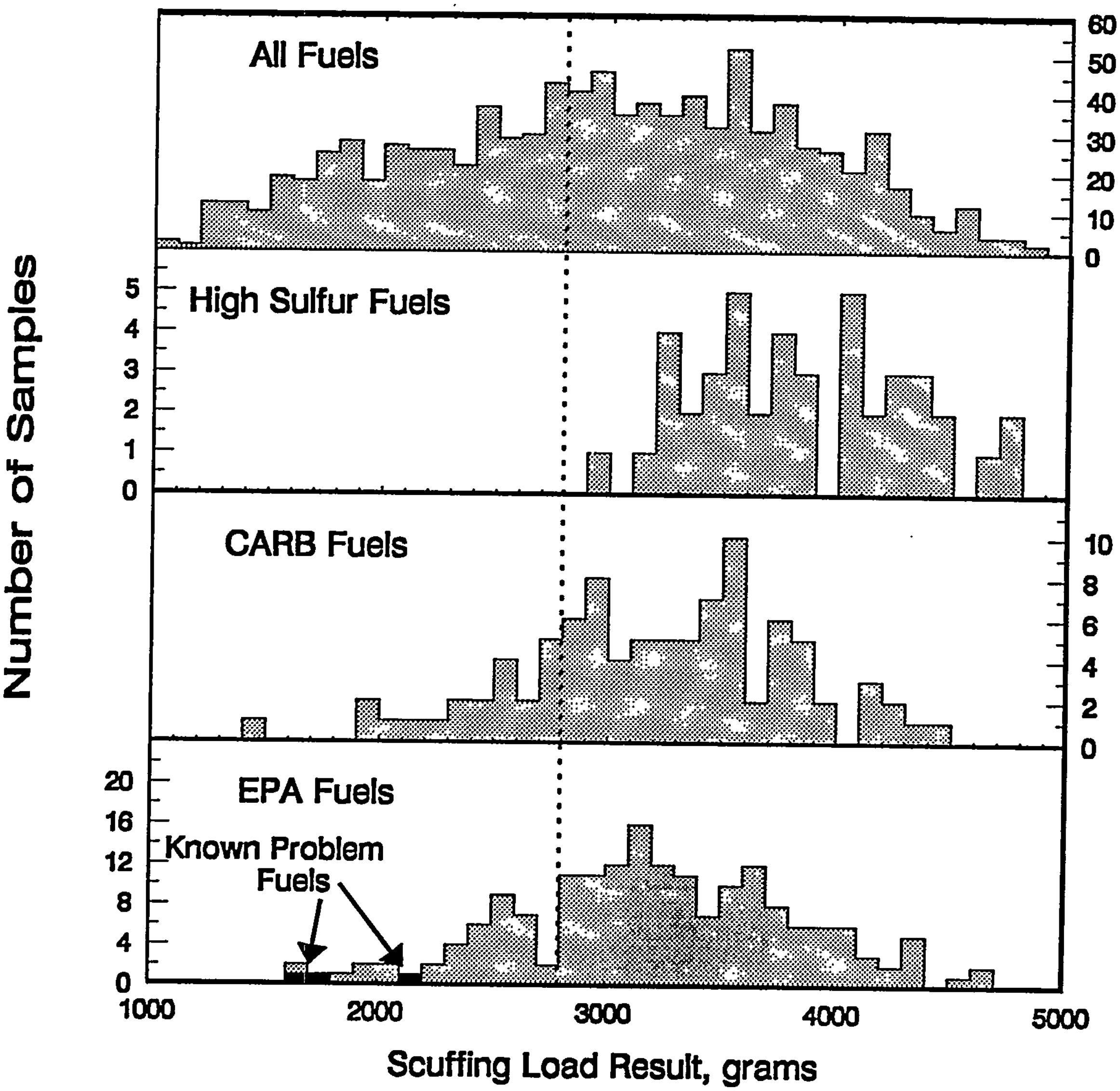
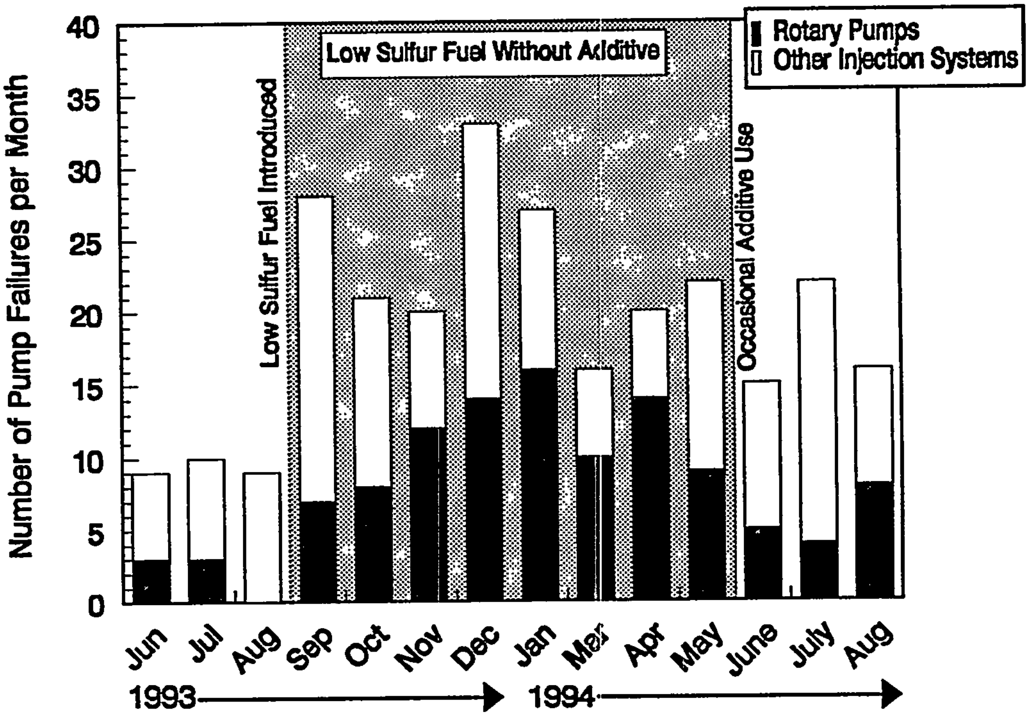


Figure 1. Histograms summarizing test results obtained using the U.S. Army Scuffing Load Wear Test for the fuel categories described in TABLE 2



(Low lubricity fuel, with a scuffing load capacity of 1,600 grams, was introduced in September 1993. Lubricity additives were included on a sporadic basis from June 1994.)

Figure 2. Pump failure rates recorded at a military base by month

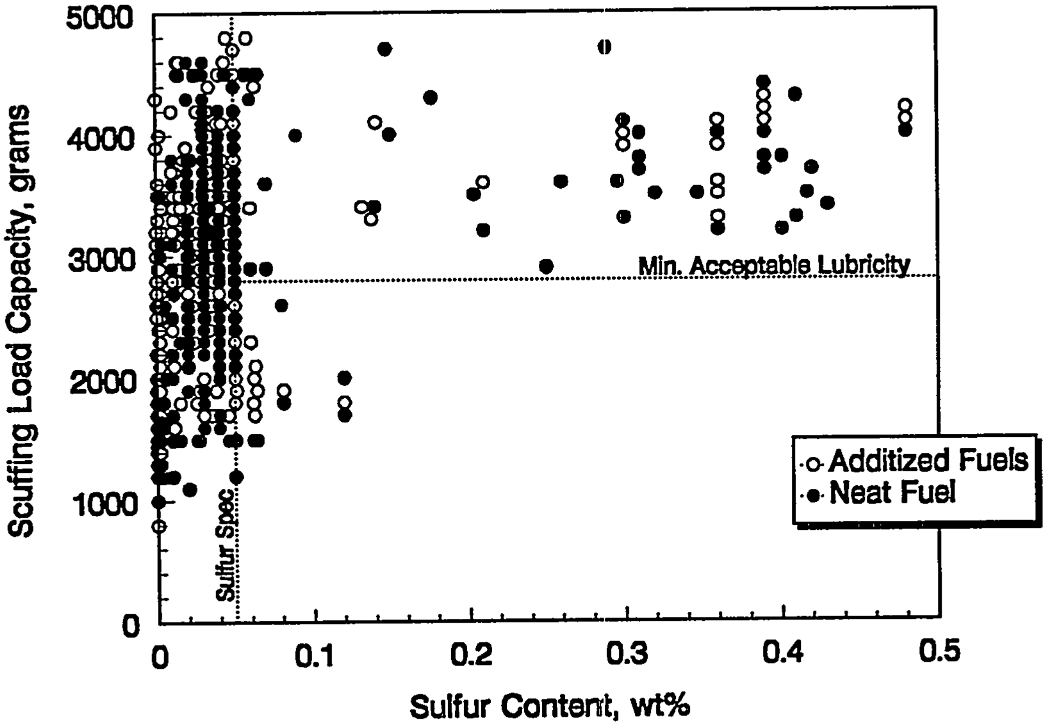
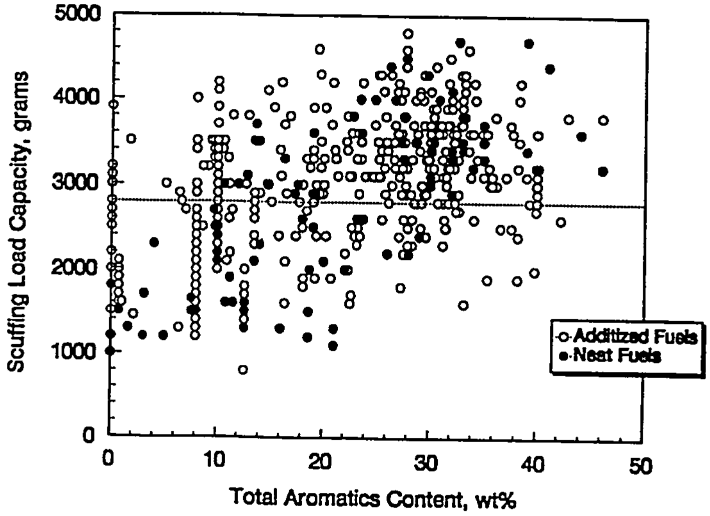
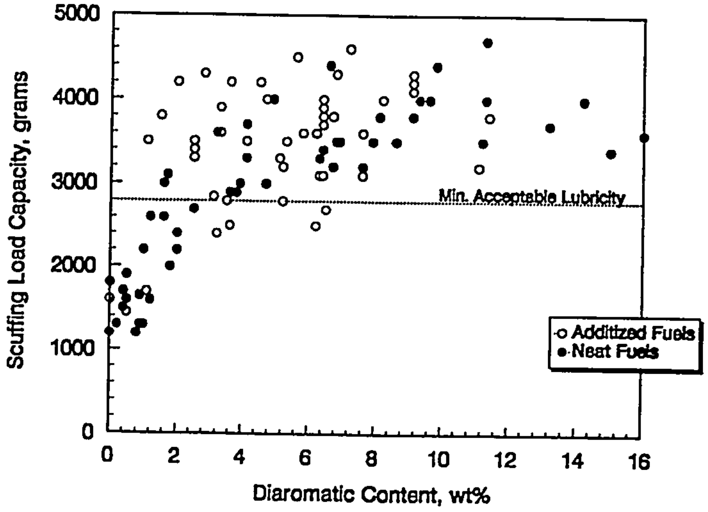


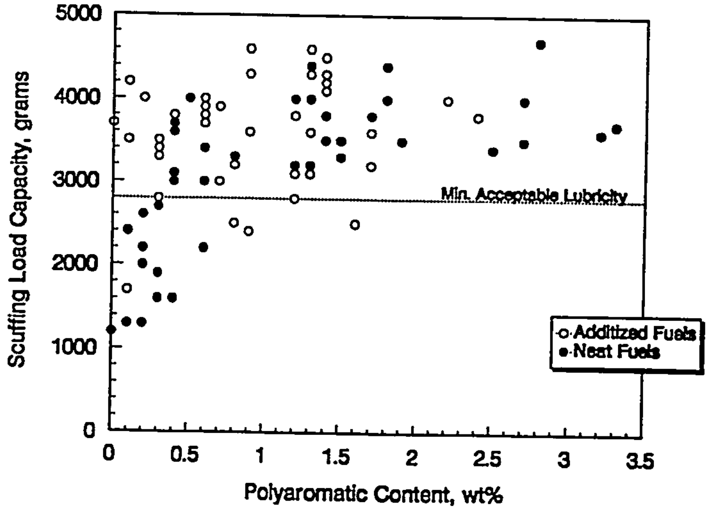
Figure 3. Correlation between scuffing load capacity and sulfur content for the complete data base, including those fuels not commercially available

a. Total aromatics content





b. Diaromatic content



c. Polyaromatic content

Figure 4. <u>Correlation between scuffing load capacity and aromatics content for various aromatics types</u>

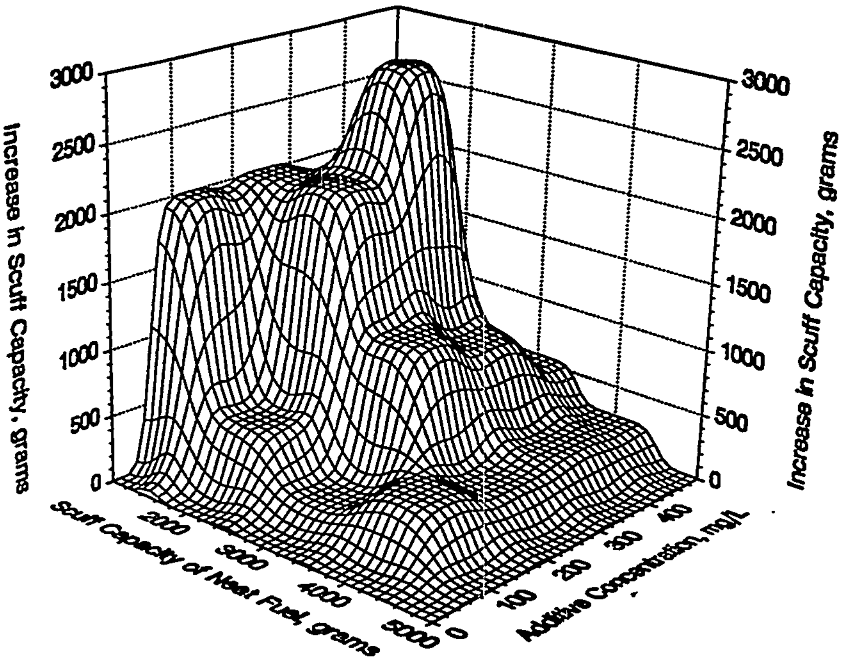


Figure 5. Increase in scuffing load capacity due to additives as a simultaneous function of additive concentration and the scuffing load capacity of the neat fuel

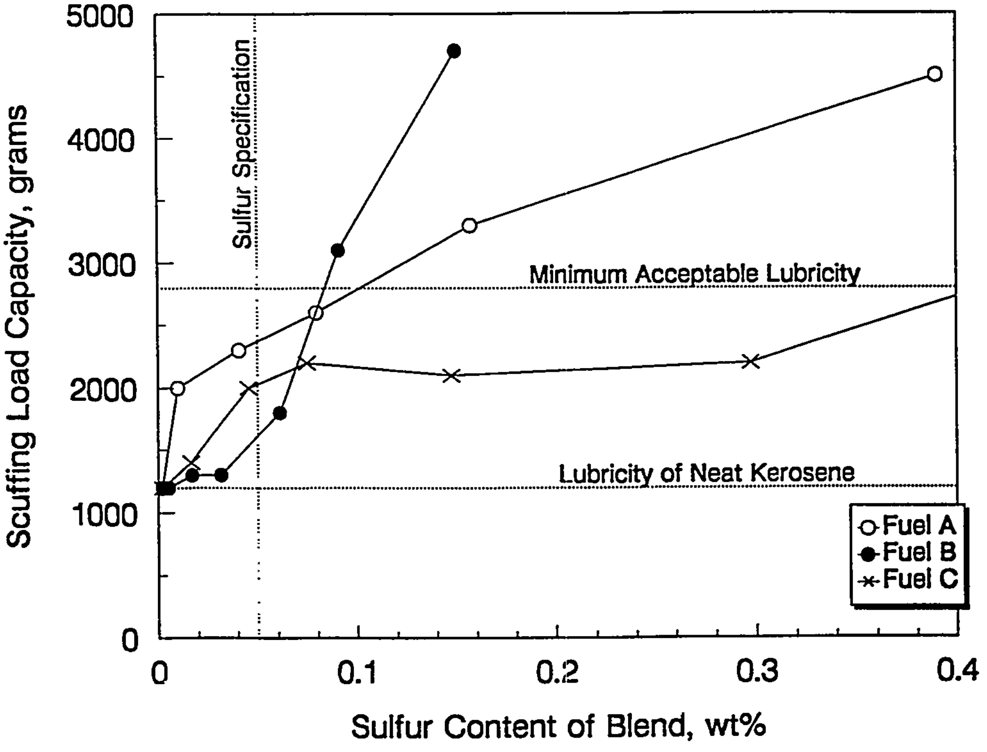


Figure 6. Effect of blending high-sulfur fuels on the scuffing load capacity of a low lubricity, low sulfur aviation kerosene fuel

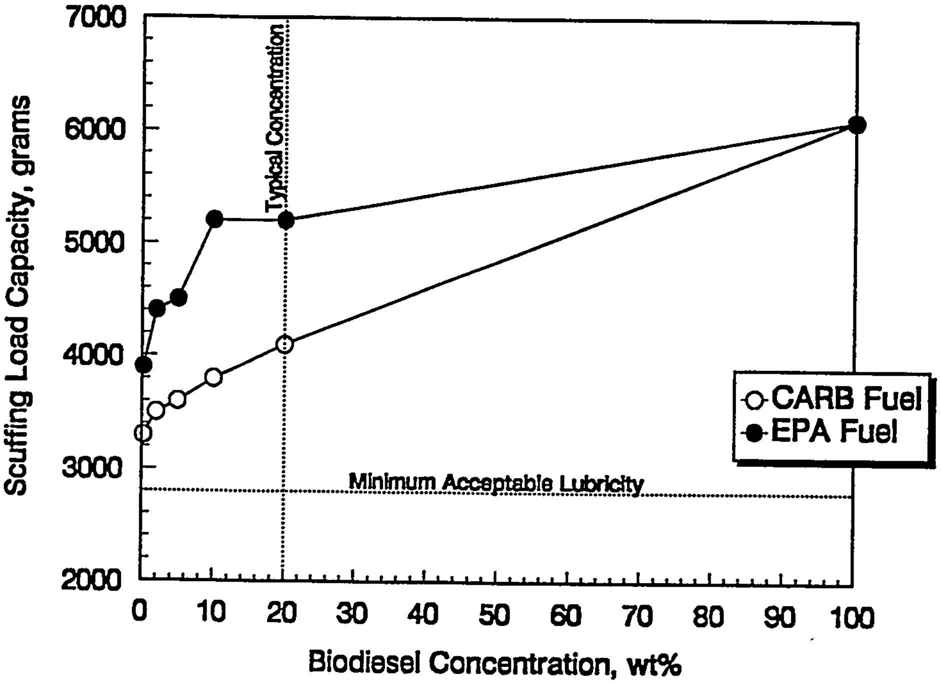


Figure 7. Effect of blending methyl ester (soydiesel) on the scuffing load capacity of good lubricity diesel fuels

TABLE 1. Fuel Classes

Fuel Class	Introduced	Maximum Sulfur, ppm	Maximum Aromatics, vol%	Minimum Cetane Number	90% Point, °C	Mean SLC*, grams
Sweden/Class I	1991	10	5	50	285 (95%)	1,200**†
Sweden/Class II	1991	50	5	47	295 (95%)	1,400**†
Sweden/Class III	1991	3,000	--	46	340	--
Europe	1994	2,000	--	48	--	3,800†
Europe/CEN	1996	500	--	49	370	N/A‡
Japan	Pre-1997	2,000	--	45	350	N/A
	Post-1997	500	--	45	350	N/A
USA/VV-F-800	Pre-1993	5,000	--	40	338	3,866
USA/EPA	Post-1993	500	35	40	338	3,243
USA/CARB	Post-1993	500	10§	48	320	3,161

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* SLC = Scuffing Load Capacity

** Later Swedish fuels that contained lubricity additives had an SLC in excess of 3,000 grams.

† Represents data obtained from a small number of samples.

‡ N/A = Not yet available

§ Fuel intended for use in California must have an aromatics content below 10 vol% unless shown to produce emissions below that of a CARB-specified referee fuel.

TABLE 2. Summary of Fuels Data Base

	Category			
Property	High-Sulfur Fuels	EPA Fuels	CARB Fuels	Complete Data Base
Sulfur, wt%				
Minimum	0.12	0.01	0.001	0.0
Mean	0.305	0.0313	0.021	0.036
Maximum	0.45	0.05	0.047	0.728
Aromatics, wt%				
Minimum	18.1	0.01	5.1	0.0
Mean	31.5	28.0	21.1	16.1
Maximum	44.0	42.0	39.0	65.0