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STABILISER ADDITIVE PERFORMANCE IN DIESEL FUELS AND GAS OILS MEETING NEW ENVIRONMENTAL TARGETS

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ABSTRACT

Stabiliser additives have for many years been used to inhibit sediment and gum formation in middle distillates, both to meet national specifications and to allow maximum refinery flexibility. The greater emphasis increasingly placed on air quality requires the production of fuels which not only meet the technical requirements of the end user but which also minimise exhaust pollutant levels. Clean air legislation has targeted sulphur and aromatic contents as a method of reducing noxious emissions. Both can be reduced at the refinery by hydrogen treatment but such processes can have implications for fuel stability. The effects of hydrogen treatment processes on traditionally measured fuel parameters are evaluated and the suitability of these methods for predicting field stability discussed. Potential new problems resulting from increased processing and the resultant removal of natural antioxidants are identified, and the ability of stabiliser and antioxidant additives to resolve these difficulties demonstrated.

INTRODUCTION

Traditionally produced diesel fuels and gas oils generally have oxidation stability properties related to the amount of thermally or catalytically cracked blending material they contain.

The major routes to sediment and gum formation which characterise a fuel's instability have been discussed in great detail,[1] and may be summarised as follows:

- acid-base reactions involving nitrogen, oxygen and sulphur species
- polymerisation reactions involving unsaturated hydrocarbon species.
- esterification reactions involving aromatics and heterocyclic species.

Many fuels have perfectly acceptable stability characteristics and can meet required national specifications by controlled blending of cracked and straight run components. If, however, large amounts of cracked stock, or exceptionally unstable stock are used, a situation may arise where additive treatment becomes necessary to improve storage stability. Additives which have proved successful at restricting oxidation and sediment formation in such fuels include:

- amine based stabilisers
- dispersants
- metal deactivator
- hindered phenol antioxidants.

The current trend towards producing more environmentally friendly fuels has targeted large reductions in both sulphur and aromatic contents of diesel fuel as a means of reducing exhaust pollutants. These reductions have imposed limits ranging from 0.05% wt sulphur and 35% vol aromatics in a US highway diesel, to 0.001% wt sulphur and 5% vol aromatics in a Swedish Class I city diesel. Fuel compositions meeting these limits are being achieved by severe hydrogen processing.

Although this type of treatment is effective at reducing vehicle emissions, other "side" effects are apparent. Secondary effects of this processing generally include:

- a reduction of the fuel's intrinsic lubricity
- the production of fuels with lower densities, viscosities and final boiling points
- modification of the fuel's oxidation properties.

It is this final point which will be discussed in this paper.

TRADITIONAL PROBLEMS

As previously mentioned, stability problems in diesel fuel generally arise as a result of cracked material being blended into straight run components, allowing more useful production from the barrel and thus extending distillate production.

The sediments and gums which result from oxidation reactions act to block filters and lay down deposits on engine surfaces. Additives which interfere with their production do so by two mechanisms:

- amine based stabilisers react with acidic species preferentially, sacrificing themselves to form soluble reaction products and by reducing hydroperoxides to alcohols
- hindered phenol antioxidants react with free radicals to form a stable intermediate which takes no part in further reactions, thus acting as a radical trap or deactivator.

Use of these kinds of products, along with multifunctional performance additives, dispersants and metal deactivator, has led to improvements in observed stability and has resulted in refiners being able to extend the diesel pool through the use of even more cracked stock.

Other antioxidants, such as aromatic diamines, whilst being more effective than hindered phenols as radical traps in gasoline, have not been used in diesel fuel because they participate in side reactions, forming sediments by different mechanisms.

CURRENT AND FUTURE PROBLEMS

The hydrotreating necessary to significantly reduce sulphur and aromatic levels to within the new specification limits will also act to reduce the concentration of nitrogen and oxygen species and even olefin levels in the fuel.

These reductions will have an obvious impact on the amount of sediment and gums generated and will result in the production of fuels which appear to have excellent stability characteristics as measured by the current techniques.

Not all the polar species contained in fuel, however, are detrimental to its stability. Certain compounds act as natural oxidation inhibitors and it is the removal of these beneficial species through hydrotreatment processes that could have an unforeseen impact upon fuel stability. Removal of these radical traps may result in the production of large amounts of hydroperoxides which, in addition to aiding free radical polymerisation, have a significant effect upon elastomers present in vehicle fuel systems.

Peroxide attack was identified as the cause of embrittlement and fracture of neoprene and nitrile rubber components by British Forces in the Far East in 1962[2]. The source of the peroxides was a hydrotreated jet fuel, leading the United Kingdom Ministry of Defence to mandate the use of antioxidant in hydrotreated jet fuel. Similar occurrences in the 1970s[3] and 1980s[4] led the US Military to follow suit, and it is now common for hydrotreated jet fuel to be antioxidant treated.

Potential to form peroxides in low sulphur diesel fuel will not be serious in the majority of cases. Most fuel will be consumed before major peroxide formation occurs but there will, however, be a small proportion which will go to storage. In long term storage, the opportunity to form significant amounts of peroxide will occur.

Work to evaluate both the peroxide forming tendency and the traditionally measured stability of low sulphur fuels has been performed. The ability of additives to control peroxide formation and enhance stability in these fuels has been assessed.

FUELS USED FOR TESTING

Twenty nine fuels were evaluated in total and are categorised as follows:

- three Swedish Class II fuels (0.005% wt max S) Fuels 1 to 3
- three proposed future European fuels (0.05% wt max S) Fuels 4 to 6
- twenty one US low sulphur fuels (0.05% wt max S) Fuels 7 to 27
- two current European fuels (0.3% wt max S) Fuels 28 to 29

Physical property details for the European fuels are given in Table 1.

TEST PROCEDURES

Two distinct types of analyses were performed:

- peroxide formation tests
- conventional fuel stability tests.

Details of the methods employed are given below.

Peroxide formation tests

Two procedures were evaluated:

- oxygen overpressure bomb tests

  ASTM D525 test equipment was prepared for use according to the D525 procedure.

  100 cm^3 of fuel was introduced and each bomb pressurised to 724 mbar with oxygen or 2413 mbar air.

  The fuels were then aged at 100°C for 24 hours. After ageing, the bombs were de-pressurised, and the sample quenched in ice water for ten minutes.

  Following this, the samples were analysed for peroxide content by ASTM test method D3703, (Peroxide number of aviation turbine fuels), or the PERFECT analyser (Automatic peroxide number apparatus)

- extended storage 65°C tests

  Tests performed according to the Co-ordinating Research Council (CRC) procedure [5] except that sample size ranged from 100 cm^3 to 150cm^3.

  Following this, the samples were analysed for peroxide content as previously described.

Conventional fuel stability tests

Some of the European fuels were evaluated for sediment and gum forming tendency by ASTM D2274 and Du Pont F31A procedures.

TEST MATRIX

Analyses performed were as follows:

- 24 hr bomb tests - All fuels
- 65°C tests - Fuels 2, 5, 6, 8, 13, 14, 15, 16, 17
- ASTM D2274 - Fuels 2, 18, 19, 20
- DuPont F31A - Fuels 2, 18, 19, 20

Various additives were also evaluated in several of the fuels. The additives tested comprised:

Additive 1 -	N,N^1-di sec butyl-p-phenylenediamine
Additive 2 -	N,N-dimethyl cyclohexylamine
Additive 3 -	>72% wt 2,4-dimethyl-6-tert butyl phenol <28% wt methyl and dimethyl butyl phenols
Additive 4 -	>75% wt 2,6-di tert butyl phenol <25% wt tert and di-tert butyl phenols
Additive 5 -	Amine based stabiliser.
Additive 6 -	2,6 di tert butyl-4-methyl phenol
Additive 7 -	N,N'-di salicylidene-1,2-propane diamine (metal deactivator)

The additive response test matrix comprised:

Fuel	24 hr Bomb Test	65°C test	ASTM D2274
1	Additives 1,2,3,4		
2	Additives 2,3,4,5	Additives 1,2,3,4	Additives 1,4
4	Additives 1,2,3,4		
6			Additive 1
7	Additives 1,2,3,4,5		
9	Additives 1,2,3,4,5	Additives 1,2,4,5,6,7	
16		Additives 1,2,3,5,6	
20		Additives 1,2,4,5,6	
28			Additive 1

TEST RESULTS AND DISCUSSION

The results of the analyses are detailed in Tables 2 to 9 and are averages of duplicate or triplicate testing. It can be seen that results from the accelerated bomb ageing procedure are markedly different for those analyses performed in Europe from those performed in the US. While both sets of data show the test to be suitable for screening fuels for peroxide formation, severity of test and judgement of suitability for additive assessment differed considerably. It is considered, therefore, that the test should probably be used only for screening basefuels and that additive performance testing should be restricted to the 65°C CRC procedure.

Nevertheless, it is apparent that the fuels produced for the Swedish market (1 to 3) exhibit extremely consistent peroxide forming tendencies and that they are expected to exceed the generally accepted maximum level of 8 ppm peroxides after 4 weeks at 65°C.

The remaining low sulphur fuels show much more variation in their peroxidation with levels ranging from 0 to 168 ppm peroxides after 24 hour bomb testing. Significant variation of peroxidation in US fuels has been observed previously.[6] Although restricted to one data pair, it is interesting to note that Fuels 8 and 9 are identical except that Fuel 9 contains a multifunctional detergent/cetane improver additive. It appears that this additive treatment increased the level of peroxides formed after 24 hours from 0 to 168 ppm. The European current production fuels, as expected, produced no peroxides.

Although 24 hour bomb testing of the US fuels showed this procedure to be unsuitable for additive response testing, overall the trends observed are extremely consistent. Additive performance can be summarised as follows:

- Additive 1 (phenylenediamine) best additive
- Additives 3,4 and 6 (hindered phenols) next best
- Additives 2 and 5 (amine stabilisers) least effective
- limited testing shows Additive 7 (metal deactivator) aids antioxidant performance.

Results from more traditional analyses demonstrate that all tested fuels possessed excellent stability characteristics. This implies that the methods currently used to test for fuel stability may not be suitable for the new generation of low sulphur fuels.

What is also shown, however, is that Additive 1 does not significantly reduce the stability of these fuels and thus could be considered for use as an additive in future diesel, whereas it was found unsuitable previously in standard diesels.

CONCLUSIONS

Work performed for this paper has demonstrated that:

- fuels produced currently for use in Scandinavia and the USA, and those which are likely to be produced to conform to the future European specification, may have a tendency towards formation of peroxides
- the 24 hour bomb test is suitable for screening fuels but may not be suitable for performing additive response testing
- traditional additives such as amine stabilisers fail to control peroxide formation adequately
- phenylenediamine type antioxidants are more effective then hindered phenol antioxidants in neutralising peroxides
- effective treat rates for phenylenediamine antioxidants are in the range of 2 to 10 mg/l
- phenylenediamine type antioxidants do not promote instability in low sulphur fuels to the extent reported in traditional diesel fuels
- the PERFECT analyser is suitable for measuring peroxide content of diesel fuels.

It is felt that peroxide formation could cause problems in low sulphur fuels destined for any form of long term storage.

Slight differences in crude source or processing severity could significantly influence the peroxide forming tendency of the finished fuel, and thus it may be prudent to consider routine additive use in fuels produced by the deep hydrotreatment required for low sulphur, low aromatic levels.

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Table 1
Product quality of fuels

Property		Fuels							
		1	2	3	4	5	6	28	29
Density, g/cm^3 @ 15°C		0.8158	0.8157	0.8157	0.8450	0.8469	0.8468	0.8438	0.8609
Viscosity, cSt	@ 20°C	2.5	2.4	2.6	3.9	4.6	4.2	3.8	4.8
	@ 40°C	1.7	1.7	1.8	2.5	2.9	2.7	2.5	3.0
FIA analysis	% vol saturates	81.9	82.1	81.0	67.2	68.3	65.0	70.1	62.8
	% vol olefins	1.6	1.5	0.9	1.6	1.0	1.7	1.6	1.7
	% vol aromatics	16.5	16.4	18.1	31.2	30.7	33.3	28.3	35.5
Distillation	IBP @ °C	190	181	192	174	188	179	179	184
	5% vol @ °C	202	197	204	194	206	198	195	208
	10% vol @ °C	206	201	207	204	213	209	205	218
	20% vol @ °C	211	209	213	220	231	228	221	236
	30% vol @ °C	217	215	219	236	247	244	236	250
	40% vol @ °C	222	221	225	251	260	258	250	264
	50% vol @ °C	227	227	230	266	272	271	264	277
	65% vol @ °C	236	237	239	288	291	291	285	297
	70% vol @ °C	240	240	242	295	298	298	293	305
	85% vol @ °C	254	255	256	321	325	324	321	333
	90% vol @ °C	263	264	263	333	339	336	334	346
	95% vol @ °C	278	280	277	349	366	352	350	364
	FBP @ °C	295	303	294	360	378	362	362	376

Fuels 1, 2 and 3 - Swedish Mk II diesel (<0.005% wt S)
Fuels 4, 5 and 6 - Proposed future European fuels (<0.05% wt S)
Fuel 28 - Current UK production diesel
Fuel 29 - Current UK production gasoil

(Fuel source: Conoco, UK)

Table 2
Peroxide testing
Bomb test - 24 hours @ 100 °C

Fuel	Peroxide, ppm	
	724 mbar O_2	2413 mbar air
1	7.6	-
2	7.7	-
3	7.8	-
4	17.2	-
5	6.1	-
6	0	-
7	36.5	-
8	0.4	-
9	168.0	110.0
10	1.7	-
11	1.1	-
12	0.7	-
13	1.0	-
14	0.8	-
15	-	0.0
16	-	5.7
17	-	2.9
18	-	0.4
19	-	0.4
20	-	12.1
21	-	1.4
22	-	3.7
23	-	1.8
24	-	0.9
25	-	0.3
26	-	0.6
27	-	2.2
28	-	0.0
29	-	0.0

Table 3
Peroxide testing - Additive response
Bomb test - 24 hours @ 100°C, 724 mbar O_2

Fuel	Additive	Concentration, mg/l	Peroxide, ppm
1	None	-	7.6
	Additive 1	10 30	1.9 1.7
	Additive 2	10	3.5
	Additive 3	10 30	5.2 2.9
	Additive 4	10	2.5
2	None	-	7.7
	Additive 2	10 20	7.7 5.1
	Additive 3	10 20	6.6 4.5
	Additive 4	10 20	7.0 4.5
	Additive 5	10 20	7.0 4.6
4	None	-	17.2
	Additive 1	10 30	13.3 6.4
	Additive 2	10	19.7
	Additive 3	10 30	18.4 13.4
	Additive 4	10	13.2
7	None	-	37
	Additive 1	3	25
	Additive 2	7	106
	Additive 3	5	93
	Additive 4	12	53
	Additive 5	5	143

Table 4
Peroxide testing - Additive response: Fuel 9
Bomb test - 24 hours @ 100°C

Additive	Concentration, mg/l	Peroxide, ppm	
		724 mbar O_2	2413 mbar air
None	-	169	146
1	3	33	26
2	7	148	111
3	5	168	110
4	12	160	30
5	5	266	164
None	-	-	171
4	6	-	302
	12	-	164
	18	-	21
	24	-	11
	48	-	6
None	-	-	182
1	1.5	-	7
	3	-	5
	4.5	-	3

Table 5
Peroxide testing - Additive response: Fuel 2
4 weeks @ 65°C

Additive	Concentration, mg/l	Peroxide, ppm
None	-	15.6
Additive 1	10	3.5
	20	1.4
	30	0.9
Additive 2	10	9.5
	20	7.8
Additive 3	10	9.9
	20	5.4
Additive 4	10	6.2
	20	3.8

Table 6
Peroxide testing - Additive response: Fuel 9
Extended storage @ 65°C

Additive	Concentration, mg/l	Peroxide, ppm					
		1 wk	2 wk	4 wk	8 wk	10 wk	12 wk
None	-	0.4	0.6	0.6	3.3	8.0	219
	-	0.0	0.0	0.9	0.9	22.5	419
1	1.5	0.0	-	-	-	0.0	1.8
	3	0.0	-	-	-	0.0	0.2
	6	0.0	-	-	-	0.0	1.1
	12	0.0	-	-	-	0.0	0.8
2	7	0.0	-	-	-	1.2	3.3
	21	0.0	-	-	-	0.2	2.0
4	6	0.0	-	-	-	1.4	6.2
	12	0.0	-	-	-	1.8	3.8
	18	0.0	-	-	-	1.3	3.9
	30	0.0	-	-	-	0.5	0.2
5	5	0.0	-	-	-	2.5	9.4
	15	0.0	-	-	-	1.0	2.1
6	6	0.0	-	-	-	1.6	3.0
	12	0.0	-	-	-	0.6	2.4
4, 7	6, 1.5	0.0	-	-	-	1.1	2.2
	12, 1.5	0.0	-	-	-	0.9	1.1
1, 7	1.5, 1.5	0.0	-	-	-	0.0	0.7
	3, 1.5	0.0	-	-	-	0.0	0.0

Table 7
Peroxide testing - Additive response
Extended storage @ 65°C

Fuel	Additive	Concentration, mg/l	Peroxide, ppm				
			3 wk	4 wk	6 wk	9 wk	12 wk
16	None	-	5.4	15	18.3	11.1	-
		-	10.2	17	24.3	31.6	-
	1	1.5	-	5.0	2.53	2.4	-
		3	-	2.9	1.6	1.7	-
	2	7	-	6.5	13.1	18.4	-
	4	6	-	5.1	4.7	3.0	-
		12	-	3.5	2.7	2.4	-
	5	5	-	14.9	27.5	54.9	-
	6	6	-	3.6	5.4	5.4	-
20	None	-	4.5	6.8	16.6	14.0	-
		-	9.9	9.4	15.6	10.3	-
	1	1.5	-	-	5.0	8.4	-
		3	-	-	9.7	5.9	-
	2	7	-	-	7.4	7.7	-
	4	6	-	-	16.4	9.2	
		12	-	-	15.4	6.2	
	5	5	-	-	17.7	12.7	-
	6	6	-	-	15.0	10.4	-
8	None	-	-	0.4	0.1	2.3	3.2
10	None	-	-	0.1	0.0	0.1	1.9
24	None	-	-	0.3	0.0	1.2	0.2
25	None	-	-	0.0	0.0	2.6	0.5
26	None	-	-	0.2	0.1	3.1	1.0

Table 8
Stability testing
ASTM D2274

Fuel	Additive	Concentration, mg/l	Adherent insolubles, mg	Filtered insolubles, mg	Total insolubles, mg
2	None	-	0.08	0.04	0.12
	Additive 1	30	0.15	0.00	0.15
	Additive 4	10 20	0.10 0.08	0.01 0.01	0.11 0.08
6	None	-	0.14	0.04	0.18
	Additive 1	30	0.15	0.55	0.70
28	None	-	0.15	0.03	0.18
	Additive 1	30	0.15	0.20	0.35
29	None	-	0.05	0.04	0.09

Table 9
Stability testing
7 days @ 80°C/vented bottles

Fuel	Adherent insolubles, mg	Filtered insolubles, mg	Total insolubles, mg
2	0.60	0.15	0.75
6	0.30	0.40	0.70
28	0.15	0.20	0.35
29	0.30	1.10	1.40

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US DIESEL FUEL REFORMULATION: ADDITIVE TECHNOLOGY IN RESPONSE TO CHANGING FUEL PROPERTIES

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ABSTRACT

Rules promulgated by the US Environmental Protection Agency have forced US refiners and importers to radically change their product. While gasoline has held most of the attention, the regulations covering mid-distillates are also extensive, beginning with particulate and emissions standards in the mid-1980's and ending with the reformulation rules that began in October 1993. The assessment of sulfur and aromatic content as deleterious resulted in the final rules for on-highway fuels which specify a 0.05 wt. % limit on sulfur content and a fuel cetane index ≥ 40 to control aromatics. Fuels not meeting the on-highway requirements are required to be dyed blue (later changed to red) for easy identification. Most refineries have built or converted hydrotreaters to meet low-sulfur demands. Deep hydrotreating, besides reducing sulfur may change many of the physical/performance properties of the new fuel. Issues and concerns have been raised regarding lubricity, conductivity, corrosion protection, fuel detergency, and low temperature handling properties of the on-highway fuel. Cetane number and stability could be predicted to improve. In practice, however, very slight cetane improvement (approximately 1 cetane number) is being realized. Color stability is greatly improved by hydrotreating, but the same improvement in sediment control has not been uniformly observed. While sludge formation is generally reduced, the inherent solvency of the hydrotreated fuel may also be reduced and sediments may still form. Fuel stability additives can effectively control the residual propensity for sediment formation. Hydrotreating also reduces fuel lubricity, conductivity and corrosion protection. This paper will discuss the additive technology that is effective in meeting the industry needs mentioned above resulting from the October, 1993 US diesel reformulation.

INTRODUCTION

The US Clean Air Act of 1970 and continuing subsequent amendments require the reduction of exhaust pollutants from the nation's cars, trucks, and buses. Rules promulgated by the Environmental Protection Agency on the emission quality of fuels and fuel additives have forced the fuel industry to radically change fuels produced in or imported to the US. While gasoline has received most of the attention from oil company planners, the regulations covering diesel fuels are also extensive.

Initial diesel rules began in the mid-1980's with lower particulate emission standards for trucks and buses. At that time, engine manufacturers were concerned that sulfur in diesel fuel would make it difficult to meet these new standards with trap-oxidizer technology. Research had identified sulfur and aromatic content in particular as important contributors to particulate matter.[1] Increased engine life was also demonstrated with lower sulfur fuel. To meet EPA targets, the engine manufacturers and the fuel industry jointly submitted a joint 1989 proposal to the EPA recommending that on-highway taxed diesel fuel be limited to 0.05 wt. % S content. In addition, aromatics would be controlled either by the fuel having a 40 cetane index minimum, or a 35 vol % total limit. Diesel fuels that did not meet these specifications could be used for off-highway uses and originally were to be dyed blue for easy identification. The final rule was issued in May 1992 with the entire program beginning October 1993. This program essentially split a multi-use, single product (#2 fuel, diesel, home heating oil) into two distinct markets: low sulfur highway diesel and high sulfur off highway blue diesel. The rules for dye marking were later modified such that by Sept. 1994 all non-taxed classes of diesel (high-sulfur off-highway, and low-sulfur fuels employed in non-taxed uses) will be dyed red.

Since the introduction of this program, refinery operations planners have had to determine which of several routes to follow in order to meet all the reformulation rules. Many companies with multiple refineries have chosen one or more as a "high sulfur producer" and the others as "low sulfur producers". This has minimized capital expenditures, but may have increased overall transportation costs to the market place. Others have split the two large component streams, low sulfur straight run and cracked light cycle oil (LCO), into the two products: straight run as low-sulfur fuel and stabilized LCO as high-S product. Most refiners, however, have built hydrotreaters to meet demand. Successful hydrotreating reduces sulfur to the desired levels without cracking. This provides the desired product with minimum use of hydrogen and post hydrotreater processing. Several processes and catalysts have been discussed in the literature.[2] Most long range planners expect the entire diesel pool to be a low sulfur product by the year 2000.

PROPERTIES OF LOW SULFUR DIESEL

The deep hydrotreating of diesel to achieve low sulfur fuels has changed many physical properties of the fuel. Depending on the severity of the process, some of the changes could be predicted, however others were discovered after low sulfur diesel was introduced in the marketplace. In addition to reducing sulfur, the hydrotreating can alter aromatic content, decreases API gravity (increases specific gravity), and removes many of the more reactive components of the diesel product. This has given rise to several new physical and performance related features and concerns for low sulfur diesel.

Lubricity

With the introduction of low sulfur fuels to the US there has been widespread industry concern about fuel lubricity, based on industry experience in Scandinavia with ultra-low sulfur fuels. Diesel fuel itself lubricates the moving parts of the fuel pump and injectors. Both hydrodynamic (high speed, low load) and boundary (low speed, high load) lubrication regimes could in principle be effected, however boundary lubrication has been the greater concern. Hydrotreating removes many of the reactive hydrocarbons plus the sulfur and nitrogen containing compounds that would be expected to help with boundary lubrication. Originally it was thought that the Ball On Cylinder Lubricity Evaluator (BOCLE) used in jet fuel testing (ASTM D-5001) may be indicative of lubricity in low sulfur diesel, but further tests indicated that a more severe test would be needed. Several tests have been proposed and the industry is still attempting to agree upon a laboratory test that will satisfactorily mimic field performance. The scuffing BOCLE, a modified BOCLE with higher loads, has received some acceptance in correlating pump wear with the lubricant properties of the fuel.[3] Figure 1 gives the results of scuffing BOCLE tests run on several low sulfur diesel fuels. Compared with the high-sulfur result, these low-sulfur fuels have less lubricity and may be prone to cause increased wear on engine parts. Previous work has demonstrated that fuels with less than 3000 g scuffing loads can cause increased wear in fuel pumps,[4] and most of the fuels tested are below this level (Fig. 1). Dimer acids, which have already found corrosion inhibitor and lubricity use in jet fuel have been tested, but have relatively low effectiveness.[5] Figure 2 shows a series of fuels ranked by severity of inherent lubricity, and the improvement achieved with the addition of 30 ptb dimer acid. As seen in the chart, response to additive is fuel specific. There is also concerns regarding the use of high concentrations of dimer acid in low-sulfur fuels, especially with cross contamination of products on pipeline systems. Figure 3 compares the scuffing BOCLE results of dimer acids, as a baseline standard, with new high potency lubricity additives developed at Nalco/Exxon Energy Chemicals, LP. Excellent performance in the scuffing load can be attained with these new additives at very low concentrations. Figure 4 shows that these additives are also effective in Scandinavian winter diesel fuel, which has very low inherent lubricity, and historically has been difficult to treat. These additives are non-acid based and have the additional benefit of causing minimal effects on jet fuel WSIM values, figure 5. This latter feature is of particular interest to pipeline operator industry. Jet fuel WSIM upsets have occasionally occurred from additive contamination caused by jet fuel immediately following heavily additized diesel fuel in the pipeline.

Cetane Number

Cetane number is the most critical value measured for diesel fuel. Cetane number is a measure of the compression ignition quality of the fuel. The normal specification is 40 cetane number minimum, however a 40 cetane index minimum (or 35% vol aromatics) is the current limit set by the EPA for on-highway diesel. Hydrotreating to remove sulfur can lower aromatics, and the amount is determined by the severity of the unit and feedstock determined processing variabilities. In theory this lowering of aromatics should increase cetane numbers, however in practice very slight improvement of cetane (usually less than one cetane number) is being realized.

Fuel Detergency

Fuel detergency is a growing marketplace feature of on-highway diesel fuel in the US. Its importance in Europe has had a much longer history. Loosely defined, detergency is the ability to keep fuel injectors, fuel pumps and intake systems free of deposits in order to provide optimum performance to engine manufacturers specifications. Good fuel efficiency and emissions performance of any diesel engine is strongly dependent on the proper operation of the injection system, in particular, as well as the overall engine design. The principal cause of poor injector performance is due to the formation of injector deposits, which cause the sticking of moving parts with close tolerances, and can restrict fuel passages and spray holes.

The impetus for most modern diesel engine design changes has come in response to ever tightening governmental emission standards. In the mid-1980's when US diesel exhaust particulate regulations began, some heavy duty engines were redesigned to run with higher cylinder temperatures and pressures. However, this caused an increase in injector deposit buildup, thus negating much of the benefits. In one particular engine, the design changes to improve emissions caused severe injector carboning problems such that a 15% power reduction occurred in as little as 40,000 miles of field operation. Although injector design improvements have reduced this loss to 7% power reduction over twice the length of operation, the root causes were not entirely overcome.

These problems created a strong interest in "Keep Clean" detergent fuel additive technology. Cummins Engine Co, Inc. developed an engine-stand test procedure that simulates the injector carboning phenomenon of actual field use. This has led to the development of the "Cummins L-10 Injector Carboning Test" to evaluate diesel fuel quality. This is the only test ever designed to evaluate fuel quality in a heavy duty direct injection engine. Since its inception, a superior pass in the L-10 test has become the performance standard for fuels and detergent additives in the US. (In Europe there is a longer history of injector fouling tests to evaluate fuel quality mostly for indirect injection engines. At present, the leading test method is the Peugeot XUD-9A injector coking test under development by the CEC PF-26 group.)

The L-10 test measures injector flow loss and rates deposit levels on the injector plunger after a prescribed 125 hr engine dynamometer test cycle. Figure 6 compares the L-10 test results of the standard 0.25 wt % sulfur reference fuel with that of a low sulfur (maximum 0.05 wt %) reference diesel. While the low sulfur fuel gives slightly better baseline flow values compared with the high sulfur fuel, it produces increased injector deposits as measured by CRC ratings. This result is counter intuitive as one might expect a more stable, higher cetane fuel to produce less injector deposits. A rationalization, explaining the improved flows in conjunction with much greater CRC ratings, may be that low-sulfur fuels produce more dense deposits that cause less flow restriction. Detergent additives are necessary in order to provide superior deposit control in both fuel types. The more severe deposit forming tendencies of reformulated diesel, however, require higher additive concentrations.

Fuel Conductivity

Flowing liquids build up static charges that can result in catastrophic accidents if rapidly discharged. Accidents most frequently occur during switch loading, especially when changing from high to low viscosity products. The magnitude of the charge depends on flow rate, the mesh size of any filter elements in the line, and the time interval before loading.[6] Most refinery and terminal companies have fuel specifications in the range of 25-50 conductivity units (pico Siemens/meter) at the temperature of the loading operation. In the past, conductivity concerns were most applicable to highly paraffinic kerosine and jet fuels. The deep hydrotreating to produce low sulfur diesel has now raised concerns of fuel conductivity in the new fuels. Hydrotreating would theoretically be expected to destroy many of the polar organic compounds that might help dissipate static charges. Figure 7 gives a comparison of diesel fuel from two US refineries before reformulation (high-sulfur) and after (low-sulfur) that demonstrates this expectation. The hydrotreating has drastically reduced conductivity to the 1-6 pS/m range, which has a dangerous potential for charge development. Conductivity enhancement can be provided by conductivity additives, figure 8. Response to these additives is very fuel specific, but can be quite effective at low concentration.

Corrosion Protection

Just as hydrotreating removes polar compounds that aid lubricity, these same compounds lend some natural corrosion protection to the fuel. In addition to hydrotreating, low-sulfur diesel reformulation in many cases also involves the blending of higher proportions of kerosine. If not protected, pipelines and tankage in refineries, terminals and trucks can be corroded. Corrosion protection is measured by the NACE TM0172-86 test (ASTM D665A/B) which uses carefully prepared billets to measure actual corrosion. A rating scale is assigned to each fuel (A =0% rust, B++, B+ ≤5%, B, C, D, E ≤70% rust). Most companies require a B+ or better rating to insure adequate protection. Figure 9 shows the distribution of NACE ratings of thirty-two US low-sulfur diesel fuels. While some were not corrosive, twenty of the thirty-two were found to be unacceptable. Corrosion inhibitors, added at a 1-4 ptb dose, can improve the corrosion protection of the worst fuels to acceptable levels, Figure 10.

Fuel Stability

The ability to control color and sludge formation, and the dispersal of formed sediment, have been key specification parameters in diesel fuels. Color has always been more of a cosmetic marketing issue, while sediments can lead to serious operating problems. Historically, one way to produce more stable diesel was to hydrotreat to remove the more reactive components. The other choice has been to employ stability additives. Hydrotreating to meet low sulfur targets has lead to a reduction in color formation for most fuels. However, formation of sediment has not always decreased with hydrotreating. Figure 11 gives the 300°F/90 min stability results for some low-sulfur fuels that illustrates this. While one can generally say that hydrotreating reduces sludge formation, the solvency of the fuel may also be negatively effected. For this reason some fuels will continue to produce unacceptable sediment levels and thus fuel stability additives will continue to be required for select low-sulfur fuels. Additionally, stabilizer chemistry with antioxidant properties may be of increasing need to control peroxide formation. Reformulated fuels have an increased propensity to form peroxides, which can be harmful to seals and other elastomer based materials.[7]

At the same time, stability is an increasing concern for off-highway diesel fuel. Sediment is a particular concern because these fuels are increasingly composed of higher proportions of non-hydrotreated light cycle oils (LCO) and light coker gas oils (LCGO). Much of Nalco/Exxon Energy Chemicals' recent stabilizer effort has been directed at sediment stabilization in neat streams of these cracked stocks, Figure 12. Stabilizers improve the sediment levels of these streams and in some cases approach the acceptable specifications of a finished fuel (≤2mg/100ml). Stability additives also improve sediment levels of high-sulfur fuels. The high concentration of red (or blue) dye added to these fuels sometimes increases sediment. Additive use therefore helps to retain the originally intended dyed appearance of these fuels.

Diesel Handling Properties: CFPP, Pour Point

The cold weather handling properties of diesel require careful attention from refiners during production to ensure proper fuel flow in severe weather. The Cold Flow Plugging Point (CFPP) test and the Pour Point test are used by many US refiners to establish low temperature specifications. Refiners commonly add kerosine to reduce the CFPP and Pour values. Lower density kerosine does not have the BTU content of diesel on a volume basis and lowers the mileage performance in heavy duty engines. Pour point depressants are an alternative that can be very effective for lowering CFPP and pour point while maintaining BTU content.

Hydrotreated fuel might be expected to have poorer low temperature properties due perhaps to a greater paraffinic nature. In those fuels we have examined, however, we have not noticed significant changes relative to prior high-sulfur fuels.

Figure 13 shows the response of reformulated fuels to PPD additives. Pour point depressants at modest concentrations continue to provide good performance in the low-sulfur diesels, which make these additives a continued viable alternative to kerosine blending.

CONCLUSION

The introduction of low-sulfur diesel into the US marketplace has changed many of the performance characteristics of the principal fuel, on-highway diesel. Stability properties have improved, while lubricity, detergency, conductivity, and corrosion protection have worsened. The anticipated improvement in cetane number and the expected change in low temperature handling properties have not been seen in the marketplace. Diesel fuel additives are available that will restore and even supersede the reduced lubricity, detergency, and conductivity of these fuels, as well as to ensure adequate corrosion protection for metallurgy that contacts these fuels.

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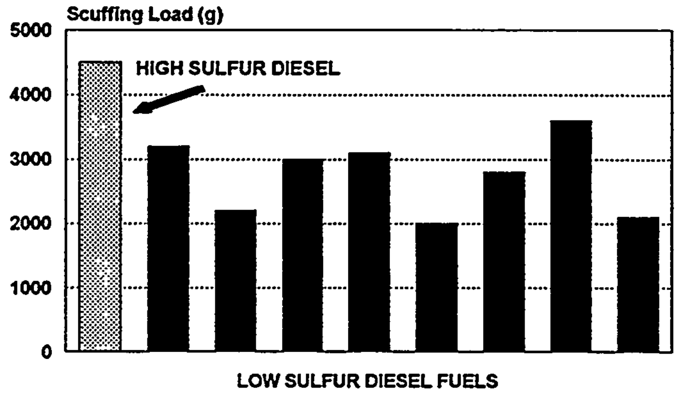
Figure 1. Fuel Lubricity Test

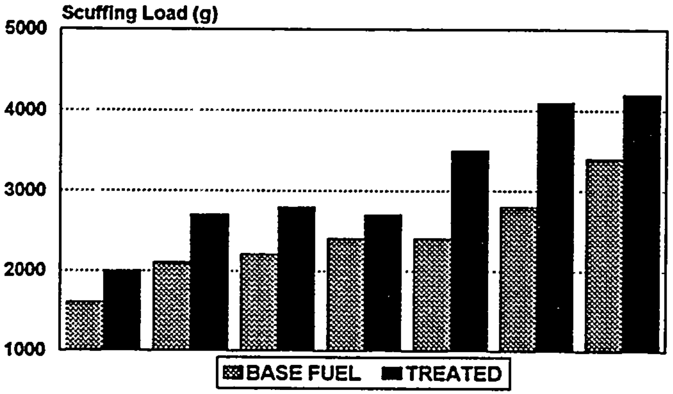
Scuffing BOCLE



NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 2. Scuffing BOCLE Tests of Low-S Diesels

Base Lubricity & Response to Additive*



*30 ptb DIMER ACID

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Figure 3. Scuffing BOCLE Fuel Lubricity Test

Comparison of Additives

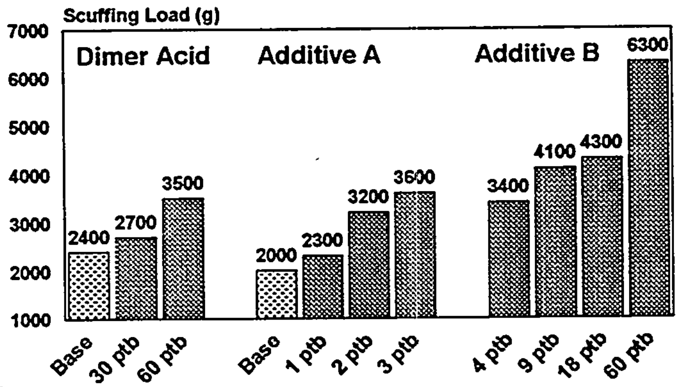

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Figure 4. Scandianavian Winter Diesel

Severe Fuel Lubricity Enhancement

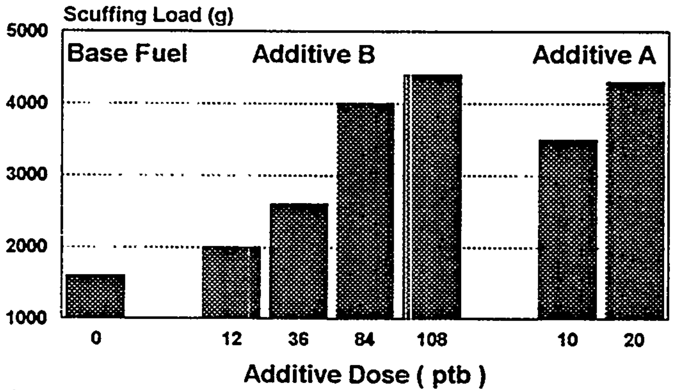

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Figure 5. Jet Fuel WSIM Test

Effect of Diesel with Lubricity Additive

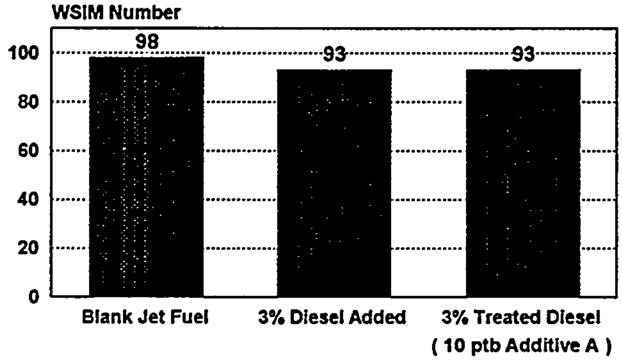

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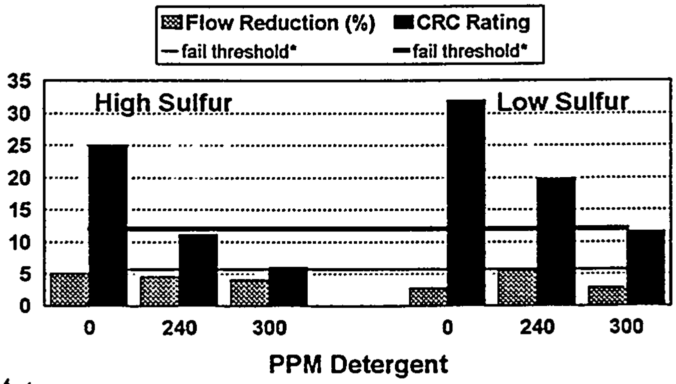
Figure 6. Diesel Detergency

Cummins L-10 Injector Carboning Test



NALCO/EXXON ENERGY CHEMICALS, L. P.

* Superior Pass

Figure 7. Fuel Conductivity

Comparison Before and After Reformulation

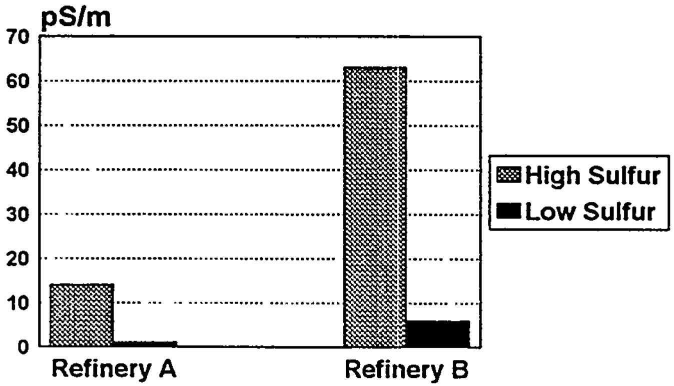


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Figure 8. Fuel Conductivity Test

Response to Conductivity Additive

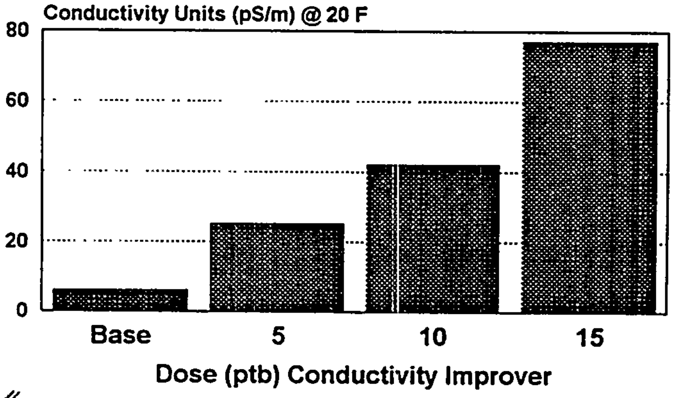

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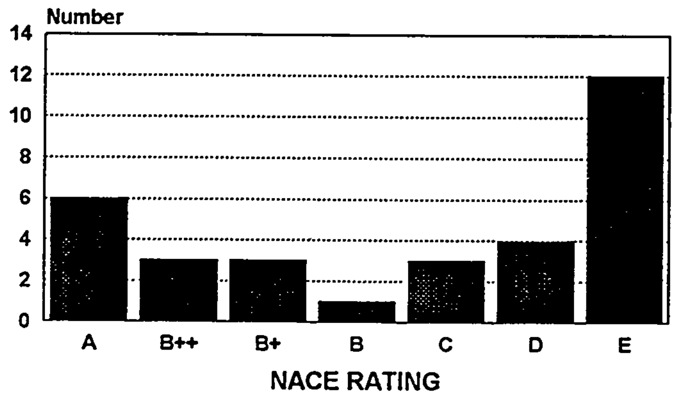
Figure 9. Diesel Corrosion Protection



Distribution of 32 U.S. Low-S Fuels

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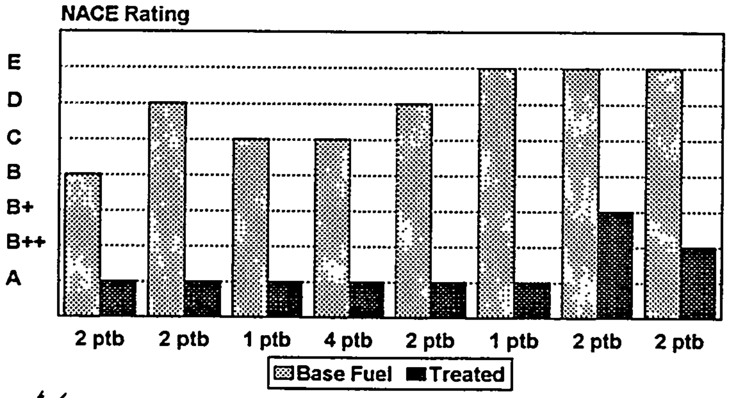
Figure 10. Corrosion Testing



Corrosion Improver Performance in Low-Sulfur Diesel

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Figure 11. 300° F / 90 min Stability Tests

Low Sulfur Diesel Fuels

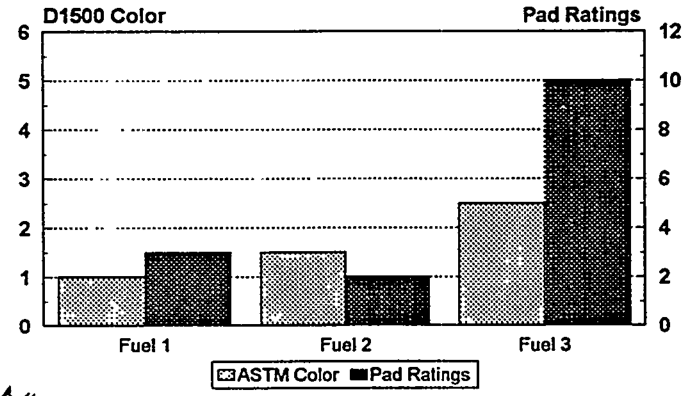

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Figure 12. Stabilization of Straight LCO's

110° F / 13 Week Stability Test

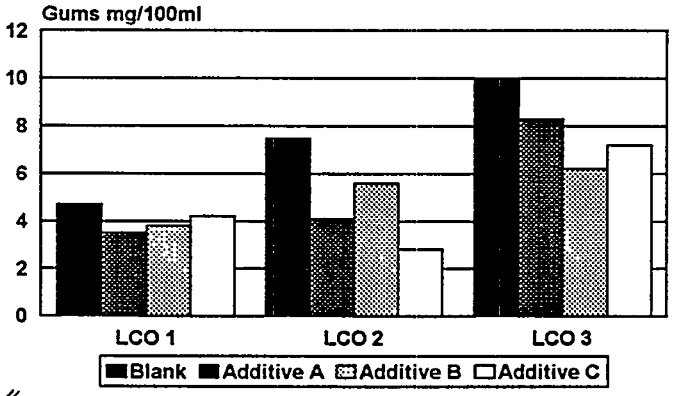

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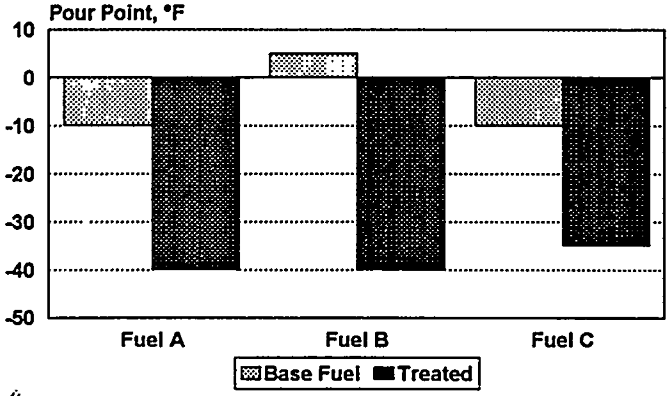
Figure 13. Pour Point Tests: Low Sulfur Fuels

PPD Additive Performance



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THE EFFECTS OF DYEING DIESEL FUEL "BLUE"

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Abstract

The recent requirement that a blue dye be added to all high sulfur, off-highway diesel fuels raised many concerns among diesel fuel users about the detrimental effects on the fuel of the addition of the blue dye. In order to assess the immediate effect of the blue dye on contamination, the Naval Research Laboratory examined 6 F-76 fuels and all 15 possible 50:50 combinations of these fuels. All fuels were filtered before dyeing to set existing contamination levels to 0 mgs/L. Each fuel was dyed with 30ppm, w/v, of blue dye and allowed to stand for 24 hours in the dark at ambient laboratory conditions. A modified D5452, "Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration" was used to gravimetrically determine the amount of filterable contamination formed in the fuels. The results of these tests, which show that the blue dye caused an immediate detrimental effect in all 6 fuels and 15 fuel combinations, will be given.

Introduction

The 1993 Clean Air Act Amendments required that beginning 1 October 1993, any diesel fuel intended for use in a highway motor vehicle must meet a maximum sulfur content of 0.05 wt.%, a minimum cetane index of 40 and a maximum aromatic content of 35%. Any diesel fuel which did not meet the on-highway (low sulfur) requirement would have to be dyed blue with 1,4 dialkylamino-anthraquinone.

A study done in 1991 at the Naval Research Laboratory, to determine the effect on diesel fuel color, indicated that the use of as little as 5 ppm of this blue dye in a dark (>4 by ASTM D1500) color diesel fuel caused copious amounts of black precipitate. This result led to concern that the use of blue dye in F-76 marine diesel fuel could potentially affect the stability of this product.

In order to assess the effects of the oil blue dye on procurement specifications, a test program was instituted to determine the frequency and magnitude of immediate compatibility problems and storage stability problems on recent production fuels.

Experimental

Six F-76 fuels, meeting the MIL-F-16884H specification requirements, were chosen for this test matrix. Two of the fuels were considered to be "typical" fuels, 2 fuels "better" than typical and 2 fuels to be "worse" than typical when compared to the requirements of the military specification. The six fuels were tested, both undyed and dyed with 30ppm oil blue dye, for immediate particulate formation and for potential storage stability. Identical tests were done on the 15 possible blends of these fuels, both dyed and undyed.

The immediate particulate formation was determined by a modified D 5452 (formally D2276) method. An aliquot of each of the six fuels was filtered to set the contamination level to 0 mg/L. These six neat fuels along with the 15 possible 50/50 v/v combinations of these fuels, blended immediately after filtering, were allowed to stand in the dark at ambient laboratory temperature for 24 hours. A 250 mL portion of each sample was filtered using two pre-weighed 0.8 micron nylon membrane filters. After completion of the fuel filtering, the filters were rinsed with hexane, dried at 70°C for approximately 30 minutes, allowed to equilibrate to laboratory conditions and again weighed to determine the total particulates. The determinations were done in duplicate and were corrected for blank filter weights and multiplied by 4 to put the results on a mg/L basis. The results determined from the 50/50 blends of these undyed fuels showed the incompatibility effects of blending alone on the amount of particulate contamination formed.

A separate set of neat fuel samples was filtered to 0 mg/L contamination and dyed with 30ppm active ingredient oil blue dye (about 60% v/v in toluene). The dyed fuels were allowed to stand in the dark at ambient laboratory conditions for 24 hours. At the end of this time the effect of the oil blue dye on particulate formation in the unblended dyed fuels was determined using the modified D 5452 method described above. Also, at this time, the

15 possible 50/50 v/v blends of the six dyed fuels were made and allowed to stand for an additional 24 hours. At the end of this storage time, the modified D 5452 method was used to determine the effect of dyeing and blending on the amount of particulates formed.

The potential storage stability of the dyed and undyed neat fuels and the 50/50 blends of dyed and undyed fuels was determined by ASTM D 5304. For this test, each fuel sample was filtered immediately prior to the start of the test to remove any existing sediment. The 100mL samples, in brown borosilicate bottles, were placed in a pressure vessel, which had been heated to 90°C in a forced air oven. The vessel was closed and pressurized to 800 kPa pressure with 99.5% minimum oxygen. The temperature was maintained at 90°C for 16 hours. At the end of this test time, the pressure was slowly released to atmospheric pressure and the vessel was opened. The sample containers were removed and allowed to cool slowly to ambient temperatures, in the dark, for at least 1 hour. When the samples had cooled, two glass fiber filters with a nominal pore size of 1.2 microns which had been weighed along with two aluminum dishes are used to filter each sample. When the fuel filtering was completed, the filters were rinsed with hexane to remove the residual fuel. The inside of each sample container was rinsed with two 15 mL aliquots of TAM (equal portions of Toluene, Acetone and Methanol) and placed in the two aluminum dishes that had been weighed with the two glass filters for each sample. The aluminum dishes were placed on a hot plate and the solvent was allowed to completely evaporate. The filters and the aluminum dishes were dried in the oven at 100°C for 4 hours, cooled to ambient temperature and weighed to determine the total amount of insoluble contamination formed.

Results and Discussion

Table 1 gives the results for 6 NATO F-76 type fuels which were supplied directly from refineries or supply depots in the United States and which had not yet been subjected to any type of blending. These 6 fuels all had existent particulate contamination as received in their 5 gallon containers. Initially an attempt was made to obtain representative aliquots from the original containers of the appropriate volumes needed in order to divide the aliquots in half and dye only one half. Then the effects of the dye on the fuel which already contained native amounts of particulate contamination (usually at quite low levels) could be determined.

Great care was taken to obtain a 1 liter aliquot from the 5 gallon containers which contained a representative concentration of existent particulate contamination. It proved too difficult to divide this small aliquot into smaller aliquots and obtain the requisite repeatability for the D5452 test necessary to determine if the dye was exerting any effect at all on immediate incompatibility as measured by particulate contamination.

Thus to determine an effect of blue dye incompatibility in each fuel, all aliquots were first filtered through a 0.8 micron nylon membrane filter. After 24 hours each undyed portion was again filtered and, in all cases, resulted in very low values comparable to the weighing blanks of 0.0 to 0.1 mg/L for particulate contamination. Thus the values in Table 1 represent the effect of adding 30 ppm blue dye (active ingredient dissolved in toluene at 60% w/v). The resulting particulate contamination was later extracted with known volumes of toluene and examined for absorbance at the appropriate visible wavelength. This showed that the solid thus isolated was not the blue dye itself.

Thus, this effect, which averages about 6 mg/L for all 6 fuels, is due solely to this small concentration of soluble blue dye in these representative fuels. This remarkable effect of the blue dye on diesel fuel is entirely out of proportion to its concentration in any given fuel. This type of effect is analogous to addition of a very acidic or basic or otherwise chemically reactive material to diesel fuel at ppm range concentrations. This supports the idea that the precursors to fuel oxidation sludge can remain in solution, perhaps as the so-called SMORS (soluble macromolecular oxidatively reactive species) as a colloidal suspension.[1] This colloid can be knocked out of solution by any parameter that perturbs the system such as heat, pH, etc.

In a realistic fuel logistics scenario, the fuel which has been dyed at the refinery will ultimately come in contact with other dyed (and undyed) products and thus it is necessary to determine whether the blue dye effect on immediate incompatibility, defined by the particulate contamination test, is operative. In Table 2 the effects of dyeing and blending on particulate contamination are examined separately and together. First the effect of blending alone is shown for three undyed 50:50 blends. Next, the effect of blue dye at 30 ppm alone is calculated or predicted by using the data in Table 1 for these three blends. Next, the actual effects of dyeing and blending together are shown based on experimental results. Finally, the effect of dyeing along is calculated by subtracting the undyed fuel blends data from the actual total particulates of the dyed blends (shown in the last column of Table 2).

Several things are apparent from a careful study of Table 2. First, there is a significant measurable effect from simply blending undyed fuels. This has been known for many years, however, the magnitude of this effect in recent years has not been systematically studied. Next, the ability to "predict" the magnitude of the incompatibility effect of dyed diesel fuels upon mixing is simply not possible. In one case (E/F) there is excellent comparability between the third and fourth column of Table 2 but A/F and D/E are much higher than predicted.

Next, the effect of blending plus dyeing is simply not additive or "predictable" based upon a knowledge of each effect individually. The situation is especially noticeable in E/F where the predicted combined effects would lead to a value almost twice the actual effect. The combined effects would be additive only for D/E, but A/F would be grossly under predicted. In other words, the major effect from blending blue dyed fuels is the effect exerted by the blue dye itself.

Because of this, we can go directly to the actual dyed fuel blending data in Table 3. This shows that the effect of the blue dye on immediate incompatibility as shown by particulate contamination is, in general, even more exacerbated. The average effect for the 15 blends is about 8.5 mg/L which is approaching the military specification maximum of 10 mg/L. Three of the 15 blends have failed the specification test, and one of these has failed it catastrophically. Only about 3 or 4 of the blend samples individually gave acceptable results with the blue dye at 30 ppm level.

Since the dye exerts such a large effect at 30 ppm active ingredient, it was of interest to see if this effect would decrease at lower concentrations. The results of adding 20, 10 and 5 ppm active ingredient blue dye to blend C/E are shown in Figure 1. These are typical of the behavior of the blue dye in other blends. High levels of solids are observed at 30, 20 and 10 ppm. These finally begin to drop significantly at around 5 ppm. It is interesting to note that the most likely explanation of this effect is in the chemical reactivity of the blue dye as measured by its pKb. The dye is a relatively strong organic base and thus might be expected to exert a strong effect, especially if the idea of a colloidal precursor dispersion is correct.

The other area of concern over the addition of blue dye to marine diesel fuels such as NATO F-76 was its potential detrimental effects on the long term storage of the dyed product and its blends. This effect was determined using the new accelerated stability test ASTM D5304. The dyed blends were prepared as shown in Table 4. It is important to note that for the purposes of this test, the blends are filtered immediately before the stress time of 16 hours. This essentially set the particulate levels to zero at the beginning of the test. Any particulates measured at the end of the test are an indication of the future solids forming tendencies of the test fuel.

In Table 4 the results for 6 typical blends are shown both undyed and dyed at 30 ppm of blue dye. It is apparent that the effect of the dye on this test is that in most cases it is either innocuous or **beneficial**. Note that the military pass/fail limit for this test is 15 mg/L and that only one test blend slightly exceeded this requirement.

The most likely explanation for this kind of an effect is that the precipitate caused by adding the blue dye which manifests itself as immediate particulate contamination is one and the same with the particulate measured at the end of the accelerated stress test. If the colloidally dispersed "precursors" to the oxidatively precipitated sludge are already knocked out of solution by the dye and then filtered out before the accelerated test begins, they can't show up at the end of the test. Thus the apparent beneficial effect of blue dye on long term storage stability has already been offset by the immediate particulate contamination problem caused by the dye.

Conclusions

The conclusions regarding the effects of the dye on the two fuel properties measured are simple and straightforward. There is no storage stability problem when the blue dye is added in high sulfur diesel fuels up to 30 ppm w/v. In fact, there is an apparent beneficial effect. Unfortunately this is offset by unacceptable levels of immediate particulate contamination caused by as little as 5 ppm of the blue dye to these fuels.

Indeed, these conclusions are made even more trivial by the fact that blue dye in all US diesel fuels will no longer be mandated (essentially they are prohibited) as of 1 October 1994.

The study itself, however, raises at least two important considerations which all future work in mid distillate fuel storage and handling should not ignore. First, that the addition of very small concentrations of chemically reactive species to filtered, freshly refined typical diesel fuels (or blends of such fuels) can lead to immediate solids levels at relatively high concentrations. The consequences of this for work on fuel additives and for laboratory studies involving the addition of proposed oxidatively reactive species such as acids is readily apparent and should not be ignored.

Secondly, that such immediate solids formation effects are demonstrated at all provides interesting clues into the true nature of the process of fuel oxidation resulting in solid products. That this effect can be demonstrated to varying degrees in different freshly refined fuels offers very strong support for the idea that the real precursors to these solid products are immediately formed colloidal suspensions and not necessarily the result of polymerization over long oxidation times followed by precipitation.

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Table 1

PARTICULATE CONTAMINATION BY LABORATORY FILTRATION
Modified D 5452
Fuels Dyed with 30ppm Oil Blue Dye
Results in mgs/Liter

Sample Designation	Total Particulates
A	8.2
B	9.0
C	4.2
D	5.8
E	6.6
F	3.4
Average	6.2

Fuels filtered to 0 mgs/Liter before being dyed. Particulate contamination was determined 24 hours after the fuels were dyed. 250 mLs of the dyed sample was filtered. Determinations were done in duplicate.

Table 2

EFFECT OF BLENDING AND OF BLUE DYEING/BLENDING ON PARTICULATE CONTAMINATION

Blends - 50/50 v/v
Dyed Fuels -30ppm Oil Blue Dye
Results in mgs/Liter

Sample Designation	Effect of Blending Undyed Fuels	Predicted Effect Based on Individual Fuel Results	Actual Total Particulates After Blending Dyed Fuels	Effect of Subtracting the Blending Effect (Undyed)
A/F	1.6	5.3	30.0	28.4
D/E	4.8	6.2	9.8	5.0
E/F	4.4	5.0	5.0	0.6

Table 3

PARTICULATE CONTAMINATION BY LABORATORY FILTRATION

Modified D 5452
50/50 Blends of Dyed Fuel
Fuels Dyed with 30ppm Oil Blue Dye
Results in mgs/Liter

Sample Designation	Total Particulates
A/B	6.6
A/C	7.4
A/D	3.4
A/E	8.6
A/F	30.0
B/C	4.0
B/D	6.6
B/E	7.8
B/F	3.0
C/D	8.4
C/E	13.0
C/F	5.2
D/E	9.8
D/F	8.4
E/F	5.0

Table 4

STORAGE STABILITY BY OXYGEN OVERPRESSURE
ASTM D 5304
16 Hour Stress Time
Results in mgs/Liter

Sample Designation	Non-dyed Fuel Blends Total Insolubles	Dyed Fuel Blends 30ppm Blue Dye Total Insolubles
A/D	6.0	6.0
A/E	7.0	5.0
A/F	6.0	3.0
D/E	7.0	5.0
D/F	18.0	9.0
E/F	7.0	3.0

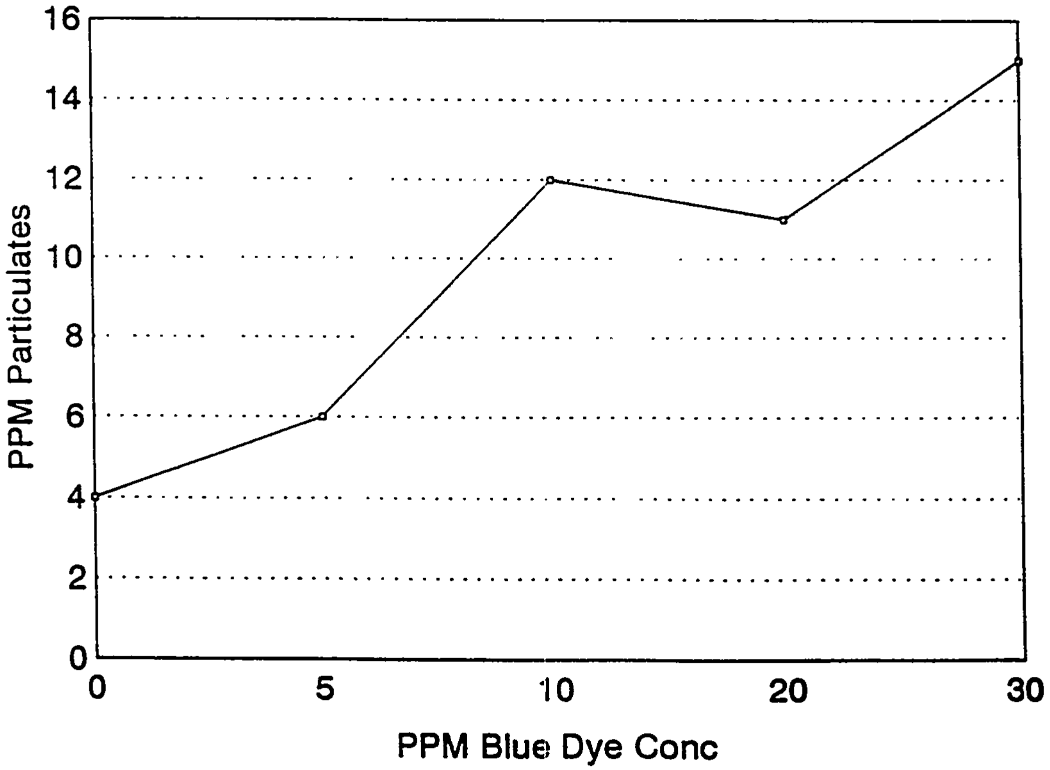

Figure 1: Average Effect of Blue Dye Concentration

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LUBRICITY CHARACTERISTICS OF LOW SULFUR, LOW AROMATIC CONTENT NAVAL DISTILLATE FUEL

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California-type diesel fuels are restricted to a maximum sulfur content of 0.05 wt% and a maximum aromatics content of 10 vol% because of environmental regulations. However, there have been instances where these fuels have exhibited low-lubricity characteristics in over-the-road diesel engine operations. The U.S. Navy may be required to use this type of fuel in the near future when operating in California coastal waters. The Navy, therefore, has initiated a program to determine the effects that the increased refining severity employed to achieve the lower sulfur and aromatic limits will have on lubricity, and hence, durability of fuel handling and diesel fuel injection equipment. Fuels conforming to Military Specification MIL-F-1688H, Fuel Naval Distillate (NATO F-76) were obtained from five refineries worldwide. This fuel is the primary fuel used in all U.S. Navy surface ships. Lubricity evaluations will employ the Ball-On-Cylinder Lubricity Evaluator, ASTM D 5001 and the U.S. Army Scuffing Load Wear Test method. A modification to the above tests may be required to account for the uniquely high salt and moisture concentration in Navy fuels before lubricity evaluations of a forty-two sample test fuel matrix will begin.

INTRODUCTION

Over-the-road diesel fuels in California are restricted to maximum sulfur and aromatics contents of 0.05 wt% and 10 vol% respectively or blends that will yield emissions equivalent to a reference fuel specified by the California Air Resources Board (CARB). These standards are being proposed for California coastal marine use as well. In the recent past, there have been instances where these fuels have exhibited low lubricity characteristics in over-the road diesel engine operations. The U.S. Navy may be required to use this type of fuel in the near future when operating in California coastal waters. As a consequence, the U.S. Navy has initiated a program to determine the effects that the increased refining severity employed to achieve the new lower sulfur and aromatic limits will have on the lubricity, and hence, durability of fuel handling and diesel fuel injection equipment. In addition, the correlation between refinery severity and lubricity will be examined, i.e., does fuel lubricity decrease linearly with increasing refining severity or does wear increase disproportionately at a critical sulfur/aromatic level?

The U. S. Environmental Protection Agency specified a maximum of 0.05 wt% sulfur content for diesel fuel over-the-road use effective 1 October 1993[1]. October 1, 1993 was the effective date for the more stringent California standards listed above[2]. The European Economic Council has set goals for diesel fuel sulfur content of 0.2 wt% by October 1, 1994 and 0.05 wt% by October 1 1996 for both marine and over-the-road use[3].

The more severe refinery processes required to remove sulfur and aromatics may result in the production of fuels reduced in the active components necessary for effective lubrication. A recent U.S. Army-sponsored study[4] has shown that there is a strong correlation between decreasing sulfur/aromatic content and wear for randomly selected diesel fuels obtained from around the world. As a consequence, increased wear may occur in the fuel handling and injection systems of both ground equipment and marine equipment that operate with these fuels. Lubricity additives are available, but there is no specification for minimum acceptable protection due to variation in additive quality or concentration. Furthermore, it has been shown in the past that fuel-related lubricity problems are fuel injection system-specific.

Two predominant wear mechanisms were observed in the Army study. The first was an oxidative process experienced with highly refined fuels that are devoid of naturally occurring corrosion inhibitors. In this wear process, a thin, weak oxide layer is formed on the contact surfaces. The weak oxide layer is repeatedly formed and removed during sliding contact to produce a high material removal rate. This material removal mechanism is quite sensitive to humidity and may increase by an order of magnitude in very damp conditions such as those experienced in water-ballasted shipboard fuel storage tanks.

The second wear mechanism observed in the above study was that characterized by adhesive wear resistance. Wear maps have indicated that adhesive wear and scuffing under high-load conditions are not directly related to wear resistance under the conditions of oxidative corrosion. Scuffing and adhesive wear, however, have occurred in high-pressure gear pumps in aviation applications and in diesel engine ground vehicles.

PROGRAM PLAN

Fuels Processing

One hundred-gallon samples of fuels conforming to Military Specification MIL-F-16884 H, Fuel Naval Distillate, NATO F-76 without additives procured from five worldwide refinery sources will be hydrotreated from small sample volumes. Sources include the United States, Spain, Israel and the United Kingdom as shown in Table 1. Little published data is available detailing the proprietary processes used by the oil companies to achieve the mandated sulfur and aromatic content. However, a recent paper by Nikanjam[5] indicates that lowering the aromatic content of diesel fuel from the traditional levels of well over 30 percent to 10 percent requires severe hydrotreating. This was corroborated by the National Institute of Petroleum and Energy Research by personal communication[6].

Hydrotreating the five fuels will be performed in a fixed-bed reactor unit containing Criterion Trilobe HDN 60 nickel-molybdenum catalyst capable of operating at pressures up to 3000 psig and temperatures up to 1000°F. Initially, a single fuel will be treated to optimize the refinery procedure. Figure 1 is a schematic diagram of the hydrotreating plant that will be employed. The feed is joined by hydrogen through a pre-heater to two fixed-bed reactors in series. Reactor effluent is cooled and liquid product is recovered in two stages of separation. Recycled hydrogen and vent gases are scrubbed to remove contaminants. The liquid product goes to a distillation column which is used as a stripper to remove H_2S or adjust flash point.

The process parameters for the hydrogenations are summarized in Table 2. The principal measure of processing severity is the liquid hourly space velocity (LHSV), an inverse expression of residence time in the reactor equal to the feed flowrate divided by the reactor volume.

For most feedstocks, sulfur can be reduced relatively easily, but the reduction of aromatics requires more severe conditions. Each of the feedstocks will be treated at a range of conditions of increasing severity (e.g., increased pressure, longer residence time) to provide four sulfur and aromatic concentrations in addition to the base fuel. Precise concentrations of sulfur and aromatics cannot be set without undergoing a cost-prohibitive number of iterations. The treatment conditions will be adjusted to produce the following four products from each feedstock:

- sulfur at 0.05 wt%
- Aromatics intermediate between starting value and 10 vol%
- aromatics at 10 vol%
- aromatics below 10 vol% (5-7 vol%)

Seven liters of each product will be made at each sulfur and aromatic content. The sulfur content will be determined using wavelength dispersive X-ray fluorescence according to ASTM D 2622. Aromatics content will be determined by supercritical fluid chromatography as defined by

ASTM D 5186 and by FIA in accordance with ASTM D 1319, the method specified by the EPA. Additional chemical analyses will be performed as necessary to define the level of severity achieved. One liter of fuel will be made available for a more complete chemical and physical analysis that will include those property determinations required by the NATO F-76 specification.

Lubricity Characterization

Laboratory Test Methods: The laboratory-scale wear tests will be performed using the Ball-On-Cylinder Lubricity Evaluator (BOCLE), Figure 2. The machine is an InterAV model No. BOC-100-007. In this apparatus, a 0.5-inch diameter AISI E 52100 ball is pressed against the rotating cylinder (SAE 8720) with a fixed applied load. The lower half of the cylinder is immersed in a bath of the fuel undergoing evaluation and the rotation carries fuel to the contact area. The BOCLE will be operated using two different test procedures: ASTM D 5001 and the U.S. Army Scuffing Load Wear Test. The principal conditions for each procedure are given in Table 3.

The ASTM D5001 test is a mild, single-load wear test. The predominant wear mechanism exhibited in this test is oxidation. Following each test for the conditions given in Table 3, the wear scar major and minor diameters on a 0.5-inch diameter ball are measured using an optical microscope, and the result is reported as the mean diameter of the elliptical wear scar formed. Figure 3 is an example of a wear scar obtained using this method.

The U.S. Army Scuffing Load Wear Test is a modification of the ASTM D 5001 test and consists of a series of incremental loads to define the applied load required to initiate scuffing. The test specimens and contact parameters were selected to provide a clear transition from mild to severe wear. Friction coefficient is also determined with the tester to better define the wear transition. Each load increment is performed over a period of one minute at a rotation speed of 525 rpm. The result is reported as the applied load in grams required to cause adhesive scuffing. The remainder of the test apparatus and the pre-test cleaning procedure is almost identical to that described in ASTM D5001. Figure 4 is an example of the wear scar for this method.

Surface Active Compounds: A 300 mL sample of each test fuel of interest will be subjected to an extraction process to determine the presence and amount of surface active compounds after a six-month induction period. It has been shown with testing of U.S. Navy JP-5 aircraft fuel samples that the surface active compounds necessary for good lubricity characteristics can return within this time period.

Laboratory Tests

Previous studies of middle distillates[7, 8] have indicated that the amount of dissolved moisture in a fuel greatly affects fuel lubricity. This effect will also be studied for F-76. Many Navy ships use seawater as ballast to replace used fuel and as a result, direct contact between seawater and the remaining fuel occurs. The effect that seawater has on the lubricity characteristics of distillates must also be evaluated.

Initially, tests will be performed using a CAT 1-H diesel fuel and a Jet A-1 fuel to determine the effects that seawater in contact with diesel fuel will have on lubricity. Using these fuels rather than the five worldwide F-76 test fuels will preserve the limited quantities of these F-76 samples available for additional lubricity evaluations. The CAT 1-H represents a good lubricity fuel while the Jet A-1 represents a poor lubricity fuel. The objective of these initial tests is to determine whether additional "Navy" laboratory test requirements are needed to account for the uniquely high salt and moisture concentration found in Navy shipboard fuels.

NATO F-76 fuel stored onboard ship may be saturated due to the environment to which the fuels are subjected. Further, free water onboard ships is acceptable up to 0.1 vol% on non-gas turbine engine combustion systems and up to 40 ppm for gas turbine engine combustion systems. As a consequence, CAT 1-H and Jet A-1 fuels with varying amounts of dissolved water, free water and seawater will be evaluated for the wear test procedures given in Tables 3 and 4. The amount of water required to reach saturation will be determined for both fuels using the Karl-Fischer method while free water will be determined using ASTM D 3241. Seawater will be prepared in accordance with ASTM D665. The results of these preliminary tests will determine if additional or modified conditions will be required when conducting the BOCLE evaluations for the five F-76 and the CAT 1-H base fuels (30 test fuels in all).

Those fuels that exhibit poor lubricity characteristics will be subjected to fuel injector/fuel pump tests to determine the effect that the two current generic lubricity additives, di- and tri-linoleic acids, will have on improving lubricity. These tests will be followed by accelerated durability tests conducted on full-size high-speed diesel engines to confirm the efficacy of the additive dosage.

Finally, both BOCLE-type wear tests will be performed to define the effect of EPA-mandated red dye on low sulfur (<0.05 wt%) fuels. Again, these tests will be conducted with the fuels whose wear characteristics are found to be the most sensitive to the reduction of sulfur and aromatics.

PROGRAM STATUS

Fuel Processing: One hundred gallon samples of the five worldwide base fuel samples have been received. Table 4 shows the sulfur and aromatic levels and other selected properties for each of the base fuels as received. Three hundred fifty gallons of CAT 1-H fuel has also been received and the hydrotreatment of this fuel to optimize the process method has begun. The hydrogenation of the five F-76 samples for the thirty-sample test matrix will not occur until the matrix testing is ready to begin. In addition, two hydrotreated fuels from each basestock will be blended with the basestock to increase sulfur content, which also simulates current refinery practice. This will result in twelve additional fuels for a total of 42 which will also be tested using the previously described tests.

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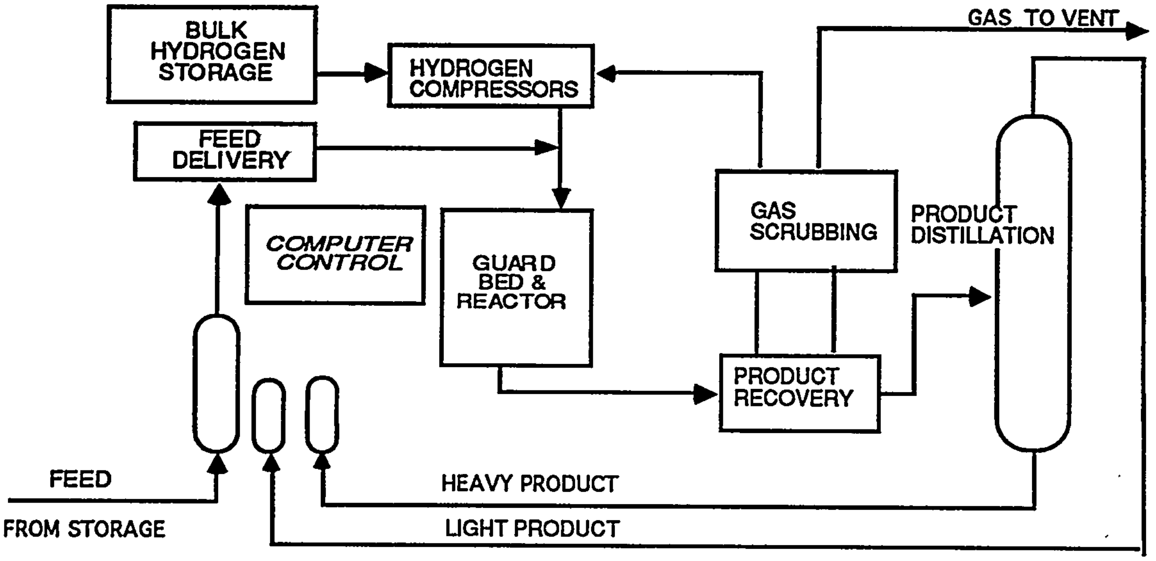

FIGURE 1: Schematic Diagram of the Hydrotreating Pilot Plant

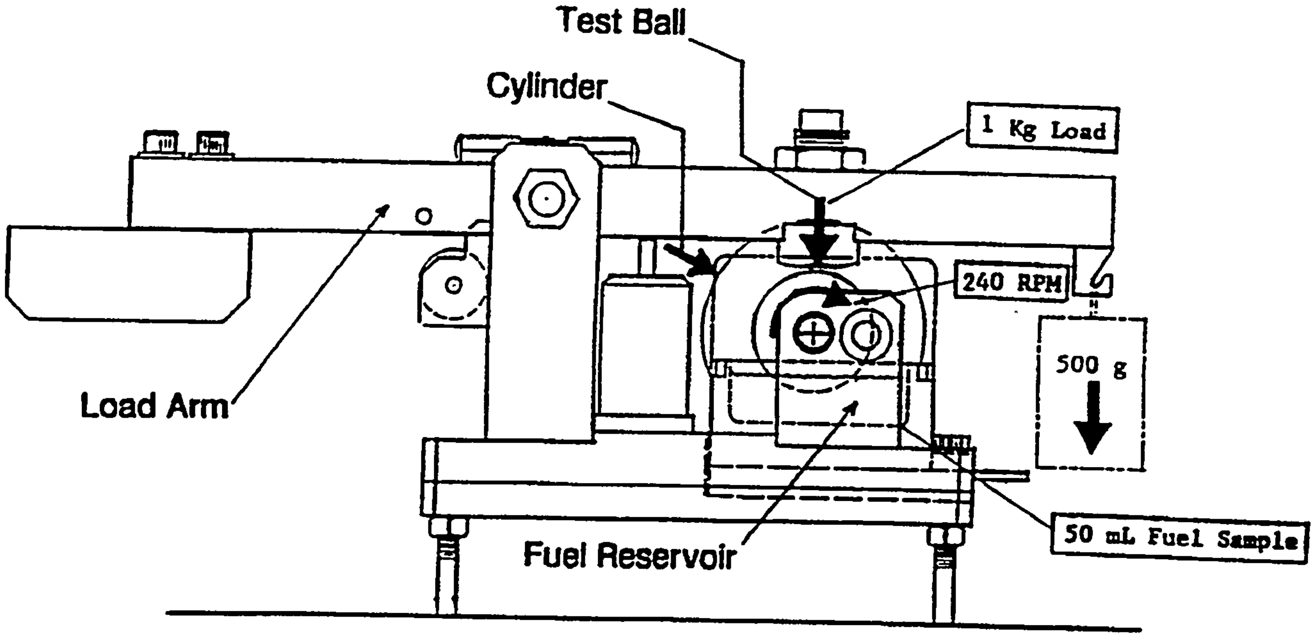

FIGURE 2: Schematic Diagram of the Ball-On-Cylinder Lubricity Evaluator

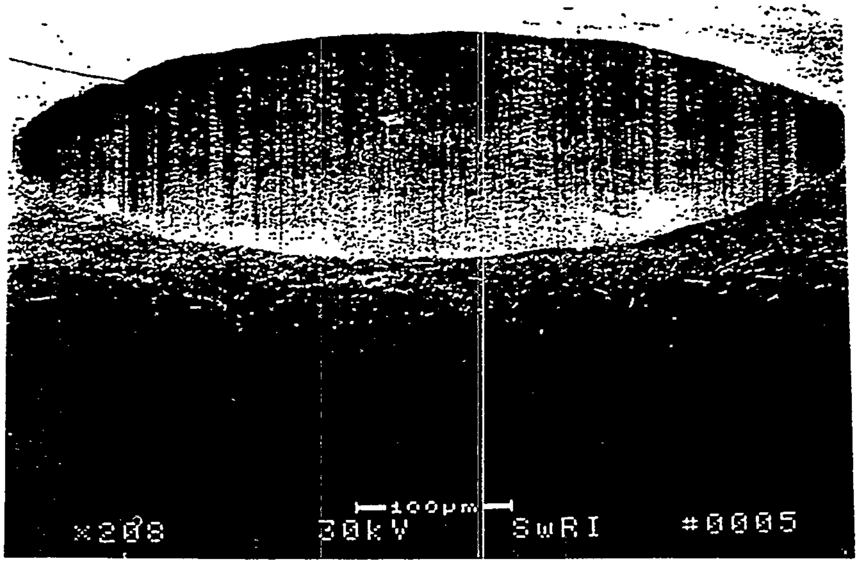

Figure 3: Illustration of a Wear Scar of the ASTM D 5001 BOCLE Test Method for a Middle Distillate Fuel.

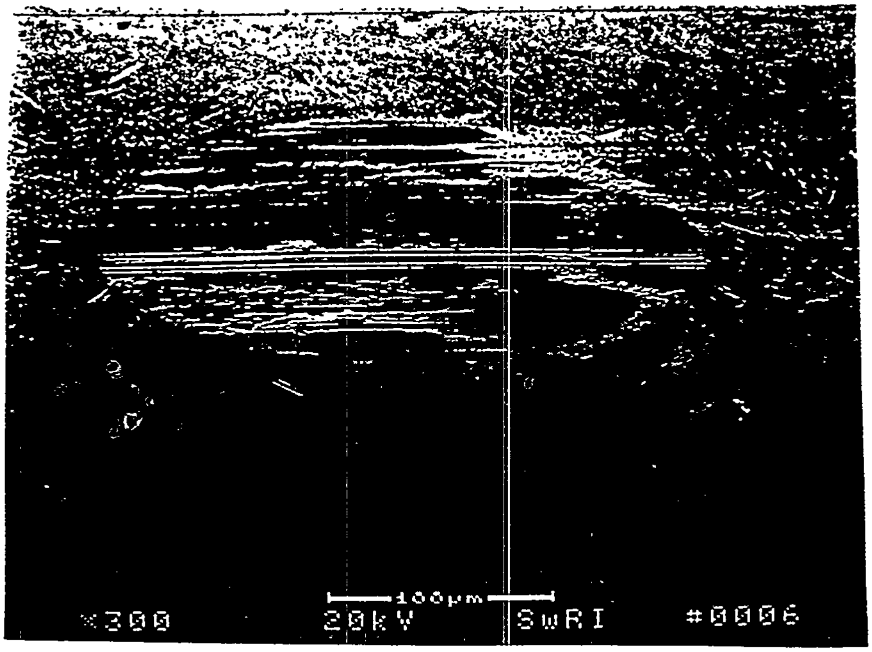

Figure 4: Illustration of a Wear Scar After Scuffing Has Occurred Using the U.S. Army Scuffing Load Wear Test Method for a Middle Distillate Fuel.

	Fuel A	Fuel B	Fuel C	Fuel D	Fuel E
Fuel Property	United States	United States	Israel	Spain	United Kingdom
Sulfur, wt%	0.41	0.51	0.89	0.73	0.14
Aromatics, wt%					
Total	27.5	33.5		26.2	39.4
Di	6.3	8.6		6.6	11.3
Poly	1.5	2.7		1.8	2.8
Cetane No./Index	49	46	51	53	47
90% Pt, °C	330	339	334	343	342
End Pt, °C	359	357	366	372	369
Flash Pt, °C	78	88	82	67	85
Viscosity, cSt @40°C	3.27	4.26	3.53	3.04	3.77
Density, kg/L	0.853	0.870	0.846	0.842	0.866

TABLE 1: Physical and Chemical Characteristics of the NATO F-76 Base Test Fuels

Item	Description	Value
1	LHSV, Hr^{-1}	1.0
2	Average Temperature, °F	630
3	Pressure, psig	600-2500

Table 2: Process Parameters For Hydrogenation

	ASTM D 5001	SCUFFING LOAD WEAR TEST
FLUID VOLUME	50 ± 1 mL	50 ± 1 mL
FLUID TEMPERATURE	25 ± 1°C	25 ± 1°C
CONDITIONED AIR	10 ± 0.2 % relative humidity	50 ± 0.2 % relative humidity
FLUID PRE-TREATMENT	0.5 L/min of air flowing through and 3.3 L/min of air flowing over the fluid for 15 min	0.5 L/min of air flowing through and 3.3 L/min of air flowing over the fluid for 15 min
FLUID TEST CONDITIONS	3.8 L/min of air flowing over the fluid	3.8 L/min of air flowing over the fluid
APPLIED LOAD		
Break-in	NA	500 g
Wear Test	500 g	500 to 8000 g
CYLINDER ROTATIONAL SPEED	240 ± 1 rpm	525 ± 1 rpm
TEST DURATION		
Break-in	NA	30 sec
Wear Test	30 ± 0.1 min	1 ± 0.1 min

TABLE 3: Operating Conditions For Ball-On-Cylinder Lubricity Evaluator (ASTM D 5001) and the U.S. Army Scuffing Load Wear Test Method.

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THERMAL STABILITY OF DIESEL FUELS BY QUANTITATIVE GRAVIMETRIC JFTOT

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Abstract

The gravimetric jet fuel total oxidation tester (JFTOT) was developed several years ago to provide JFTOT conditions which measure quantitatively the solid/deposit products formed in aviation fuels. The gravimetric JFTOT has now been used to measure these products in a small set of typical diesel fuels. These baseline data are compared to a much larger data base of jet fuels and also several pure compounds. Results from the diesels indicate that the gravimetric JFTOT is a useful concept for ranking fuels for their thermal stability. The diesels ranged from quite low (better than jet) to quite high (an order of magnitude greater than jet fuel) in their deposit forming tendencies. Properly ranked fuels can be used in device tests such as diesel injectors and gas turbine nozzles to assess deposition. In addition, diesels with appropriate viscosities may be able to be used as aviation fuels provided the gravimetric JFTOT gives a low deposition rating.

Introduction

The current worldwide standard test method for assessing thermal stability of jet turbine aviation fuels is the ASTM D3241 method. This method generates a visual tube deposit rating which is coded against color standards and the darkest color is usually said to fail a fuel for use in jet turbine engines/fuel systems. The method also generates a semi-quantitative filter pressure drop. The pressure drop is so semi-quantitative that it also is afforded a pass/fail criterion for fuel acceptance in jet aircraft.

In 1991, we described the construction of a test device which duplicated all of the experimentally important parameters of the D3241 method but which substituted a weighable 302 stainless steel (s/s) foil strip for the bulky tube, so that direct weighing of thermal surface deposits could be made.[1] In addition, the nominal 17 micron (dutch weave) s/s filter of the D3241 method was substituted with a nylon membrane 0.8 micron filter which was also capable of direct weighing of the fuel entrained solids generated by the test.

In subsequent papers, the use of this device for generating a large data base of results based on aviation fuels from many different refinery processes and many different geographic/crude sources was described.[2,3] In addition, this new device, dubbed the gravimetric jet fuel total oxidation tester (JFTOT) after the original ASTM D3241 device, was also used to assess quantitatively the effects of temperature, pressure, and fuel flow in addition to the effects of dissolved metals and various additives.

Now that a reasonable data base for jet turbine fuels has been established, regarding the deposit yields for s/s strip deposit weight and filterable deposit weight, it was of interest to see how the gravimetric JFTOT would respond to mid-distillate diesel type fuels. A suite of 7 fuels, which were similar to Number 2 diesel fuel and met all of the additional criteria of NATO F-76 (US Navy) diesel fuel, were selected for the test matrix. These fuels had originally been selected for a separate study involving long term ambient storage stability and thus were chosen in an attempt to span as wide a range of fuel properties as possible and still meet the specification requirements for military use.

Experimental

The precision flow device consists of a reciprocating, single piston HPLC pump which is connected to the fuel reservoir at atmospheric pressure on the suction side and to a high pressure filter holder containing a 0.8 micron Nylon 66 pre-filter on the high pressure side. The fuel then flows through a heated section which is maintained at the chosen test temperature by the thermostated block heater. This heated section contains the pre-weighed s/s strip (weighed to the nearest 0.001 mg on a microbalance) which is held in position by the strip holder which is assembled into the s/s tube. The fuel flows through this heated section which has a surface to volume ratio of 17 cm^{-1} at 3.0 mL/min and a residence time of 6 seconds. The fuel is cooled to room temperature and exits through a back pressure valve maintained at 3.4 mPa (500 psi) into a clean glass container.

The effluent fuel is immediately vacuum filtered through a pre-weighed 0.8 micron Nylon 66 filter (weighed to the nearest 0.01mg for the 47mm filters and to the nearest 0.001 mg for the 13mm filters). At the end of the timed test, the strip assembly is removed from the block heater and allowed to cool, while maintaining fuel flow, for about 10 minutes. The foil strip is then removed, rinsed with hexane and allowed to dry, along with the rinsed fuel filter, for approximately 1 hour at 70°C. After equilibration to room temperature, the strip and filter are weighed. The increases in weights are reported in mg/L. Exact details of the weighing technique and examples are given in previously published papers.[1-3]

Results

Seven recent production diesel fuels were tested with the gravimetric JFTOT using the standard conditions of 260°C for 2.5 hours at a fuel flow of 3.0 mL/min at a pressure of 500 psi. The results are shown in Table 1.

Figure 1 gives the ranking for the filterable deposit weights with a range from 0.9 mgs/L to 23.8 mgs/L. For comparison, the weight of filterable solids for n-tetradecane is indicated in this figure by a solid line and the maximum and minimum filterable solids weight for jet fuels tested to date is indicated by dashed lines. The ranking of the s/s foil strip surface deposit weights are given in Figure 2. In this figure the solid line indicates the strip surface deposit weight for n-tetradecane and the dashed lines indicate the maximum and minimum strip surface weights for jet fuels tested to date.

Discussion and Conclusions

The dashed lines in Figures 1 and 2 show the maximum and minimum values of the jet turbine fuels used to generate the data base in the last four years. Jet fuel average strip weights (in Figure 2) range between 0.02 and 0.20 mg/L with a number average of about 0.08 mg/L and a worldwide volume weighted average of about 0.04 mg/L. These fuels represent a very high percentage of the huge volume of jet fuels currently used worldwide and thus form a significant set of values against which to compare any and all future jet fuel batches.

The jet fuel average filterable solids weights (dashed lines in Figure 1) range between 0.5 and 8.0 mg/L with a number average of about 1.5 mg/L and a worldwide volume weighted average of about 0.8 mg/L.

Table 1 shows the data generated by the gravimetric JFTOT device for 7 representative diesel from the US. The yields of the two types of solid deposit measured are given in mg/L of fuel for both the strip weight and the filterable solids weight. It is interesting to note that even with this very small number of fuels, the gravimetric JFTOT is capable of easily distinguishing between fuels as to their tendency to form solids under the conditions of this particular test. Strip weights range between 0.00 and 0.32 mg/L with an average weight of about 0.12 mg/L. Filterable deposit weights range between 1.0 and 24.0 mg/L with an average weight of about 12 mg/L.

For the large jet fuel data base, it has been pointed out already that the filterable deposit weight is always about 10 to 20 times the strip deposit weight for any given fuel. This effect appears to be even more pronounced with the diesel fuels, where the filterable deposit weights appear to be about 100 times heavier than the strip deposit weight for any given fuel.

In order to compare the 7 diesel fuels with the jet fuel data base for thermal stability, the data in Table 1 are separated into filter deposit weights in Figure 1 and strip weights in Figure 2. In Figure 2, it can be readily seen that most of the diesel fuels exhibit very good thermal stability with respect to the strip deposit weights from the jet fuel data base. Only fuel B exceeds the heavies jet deposit weights. If this part of the test can be interpreted as the tendency of a fuel to form insulating lacquer deposits on aircraft heat exchangers, then clearly many diesel fuels are as "stable" as jet fuels in this regard.

The filterable data are shown in Figure 1, where a somewhat different picture can be seen. In this case, two of the fuels (D and E) are very good with respect to the jet fuel data base. On the other hand, two of the diesels are very "thermally unstable" (B and C) when compared to the jet fuel data base, and 3 of the diesels are "marginal" (A, F and G) being somewhat higher than the highest weights obtained for jet fuel in the past 4 years.

If the filterable weight data (or strip plus filter weight data) are used to assess the overall thermal stability performance in any given fuel, only about a third of the diesel fuels could be deemed thermally stable when compared to typical thermally stable jet fuels. It should be noted that although it is tempting to use the data in this way and call filterable deposit the material which might cause filter blockage, flow control valve sticking and nozzle fouling/clogging, no attempt has yet been made to validate this kind of correlation.

One should also note in Figures 1 and 2 the solid line which is given for the pure component n-tetradecane in the gravimetric JFTOT. This data can be used in two ways. First, it can serve as a "solvent blank" for both the filterable and strip deposit weights for jet fuels. If used in this way, it is apparent that most production jet fuels worldwide are very thermally stable indeed to the JFTOT test conditions. Secondly, it can serve as a solvent blank for diesel fuels, in which case some of the current production diesel fuels are also very thermally stable.

These results indicate that the gravimetric JFTOT is a useful concept for ranking diesel fuels for their thermal stability. The diesels ranged from quite low (better than jet) to quite high (an order of magnitude greater than jet fuel) in their overall deposit forming tendencies. This type of information can be used in 2 possible ways. First, if gravimetric JFTOT data can be correlated to such phenomena as diesel engine injector fouling, it could be used to assess any given diesel fuel's thermal stability for the intended diesel engine application.

Second, and more provocative, this type of information on diesel fuels could be used by commercial, or in some cases, by military aircraft operators to assess the thermal stability application for aircraft use. This would be subject to a given diesel fuel's suitability in all other aspects in addition to thermal stability. Various additional areas where diesel fuel might be limited would be the higher viscosity and higher freeze point/cloud point of diesel fuel which would then preclude the use as aircraft fuel. The obvious advantage, especially to long distance aircraft, would be the extended range possible with the usually higher density diesel fuel on volume limited aircraft.

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Table I. Insolubles Formed From Diesel Fuels After Gravimetric Testing. All weights in mg/L of fuel. Test conditions of 260°C, 3.0 mL/min for 2.5 hours

Fuel	s/s Strip Weight	Filter Weight	Total Weight
A	0.23	13.6	13.83
B	0.32	23.8	24.12
C	0.16	21.1	21.26
D	0.01	0.9	0.91
E	0.02	1.8	1.82
F	0.00	8.2	8.20
G	0.08	14.8	14.88

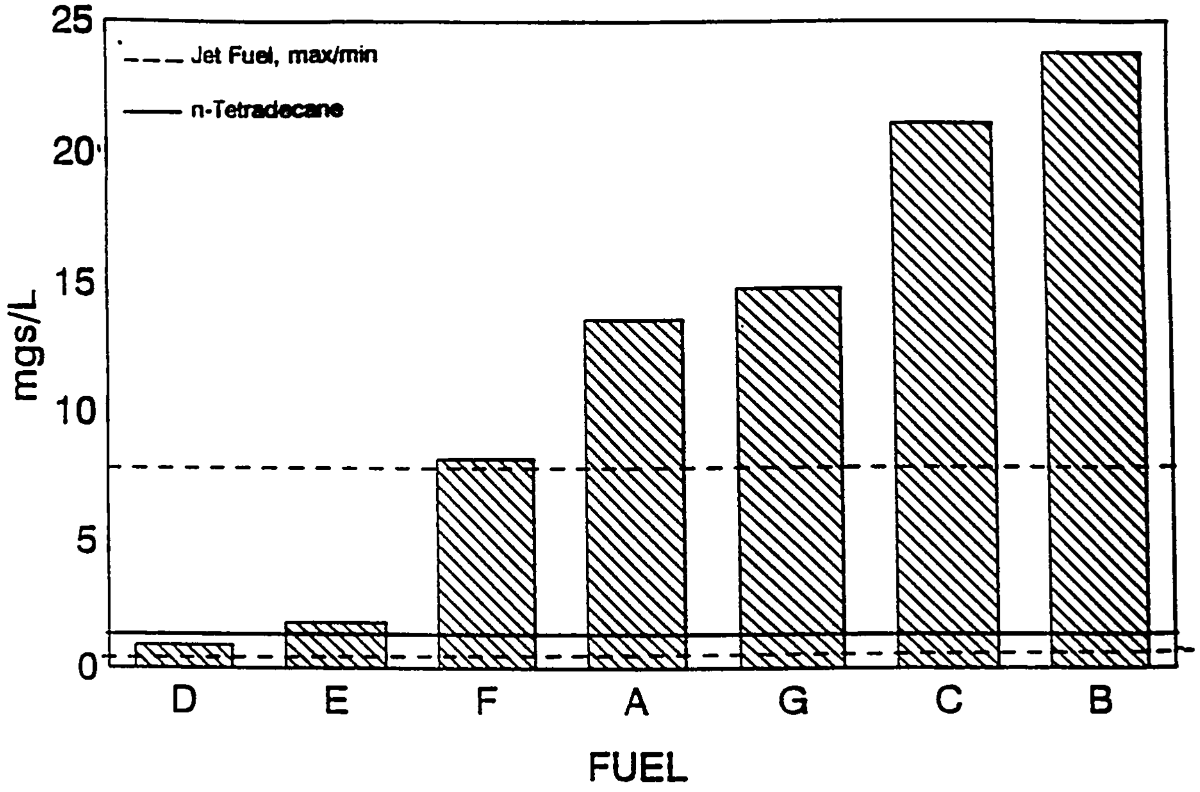

Figure 1 - Gravimetric JFTOT Filter Weights
Seven Diesel Fuels

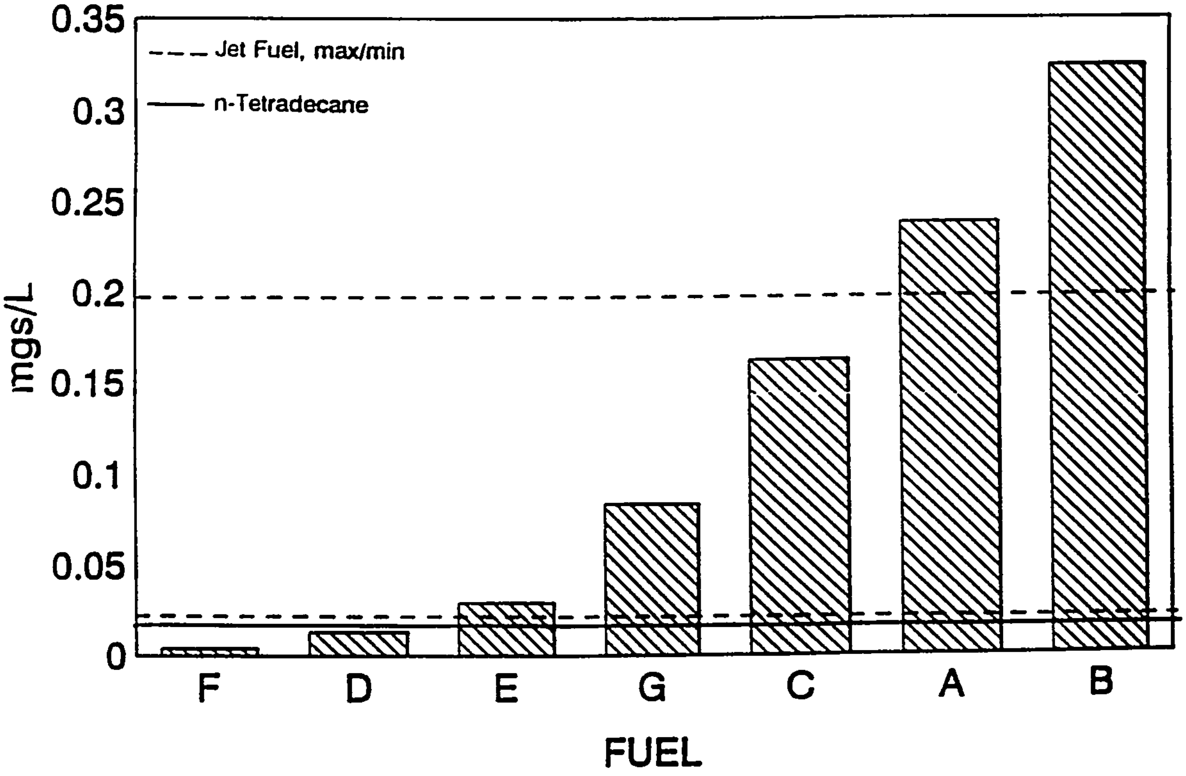

Figure 2 - Gravimetric JFTOT S/S Strip Weights
Seven Diesel Fuels

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STABILITY OF LIGHT STRAIGHT RUN DIESEL FUEL DURING LONG TERM UNDERGROUND STORAGE IN SMALL SIZE STEEL TANKS

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ABSTRACT

Three batches of Light Straight Run Diesel Fuel (LSRDF), dyed by a green marker, were stored for five years in precleaned 50,000L, steel, cylindrical, underground storage tanks, with or without biocide and a stabilizer additives package. During this period, the fuels were kept dormant and no draining operations were performed. A close follow up on the chemical properties, biocide content and the level of microbial contamination, in the stored fuels, was done throughout the storage experiment. The chemical properties of the untreated fuel remained unchanged but the microbial contamination in 'bottom-bottom' samples gradually increased during the first year and remained high for the next four years. In contrast, no microbial activity was found in the treated fuel tanks. However, in the fuel treated only by biocide, the dye green marker gradually diminished while 'acidic' odor emitted, however the fuel stayed within chemical specifications range. Fuel treated with stabilizer additives package kept its chemical properties unchanged for the five years storage. The results indicated that untreated LSRDF can be stored for at least five years without any significant microbial or chemical damage, provided good starting condition and no turnover taken place. The biocide treated effectively hindered microbial activity but enhanced a slight oxidation activity in the fuel. Stabilizer additive addition prevented this minor oxidation, while keeping the fuel and the storage tank free from microbial contamination.

1. INTRODUCTION

Microbial contamination and chemical deterioration may develop in storage tanks during hydrocarbon fuel storage [1,2]. Fuel deterioration might be enhanced in small storage facilities (up to 1,000,000L), mostly due to increased surface to volume ratio, and thus enhanced exposure to ambient conditions.

Light Straight Run Diesel Fuel (LSRDF), having a pour point -15°C has been routinely used in Israel, as winter Diesel fuel for high speed Diesel engine.

Due to its high chemical stability, LSRDF customarily stored for long terms. However the long term storage of this stable fuel was limited to two years.

Longer storage periods in tanks where form, small size and exposure to extreme climate conditions combined, were not recommended. Past experience has shown that storing LSRDF under such conditions enhanced the development of heavy microbial contamination which led to engines stalling in fields operations [3].

Results of an extensive laboratory study on the effect of several biocides and fuel additives on the kinetics of chemical and microbial deterioration of LSRDF suggested that it is possible to prolong the fuel storage period by addition of biocides and/or stabilizing additives package to the stored Diesel fuel. The aim of the present study was to determine the maximal safe storage period of LSRDF treated with additives in 50,000L steel, underground tanks.

2. MATERIAL AND METHODS

2.1. Storage tanks:

Three 50,000L, steel, cylindrical, underground storage tanks, deviated in angular toward the drain valve, were applied in this study. The tanks' dimensions were: 10m long and 2.5m in diameter. The fuel was delivered from the tank without filtration, through a low side outlet pipe located close to tanks bottom.

2.2. Diesel Fuels:

2.2.1. Light Straight Run Diesel Fuel (LSRDF 1), pour point -15^{0}C.

2.2.2. LSRDF 2, pour point -15^{0}C supplemented with 200 ppm of an isothiazolin based biocide [4], approved as a constituent of Diesel fuel additive under MIL-S-53021, [5].

2.2.3. LSRDF 3, pour point -15^{0}C supplemented with 200 ppm biocide, as mentioned in previous clause and 100 ppm stabilizer additive [6].

2.3 Growth media and organisms:

2.3.1. Trypticase Soy Broth without dextrose (TSB, BBL cat # 11774) 27.5 g/L was used in the biocide bioassay for growing the indicator bacterium *Pseudomonas aeruginosa* strain G9 (from department collection).

2.3.3. BH mineral medium, was described by Bushnell and Hass [7], used for enumeration of hydrocarbon utilizing bacteria and molds.

2.4. Additives dosing:

The biocide and stabilizer additives were supplemented into Diesel fuels in small measured portions during tanks refueling.

2.5. Diesel fuel sampling:

Sampling for microbiological analysis involved sterilized samplers and bottles, as described by Fass and Miller [8]. The sampler was immersed in the stored fuel, through a 4" valve located on the tanks' roof. The Diesel fuels samples were kept in sterile bottles, in the dark, for 24h prior to analysis.

2.6. Microbiological analysis of Diesel fuel samples:

Aerobic hydrocarbon utilizing bacteria and molds were counted by inoculating aliquots of 1 ml and 10 ml of Diesel fuel samples into 25 ml vials that contained sterile mineral medium (BH) at pH 5.6 and 7.2 and plugged by cotton stoppers. The vials were vigorously shaken then statically incubated for six days. The mold colonies developed in the interface of vials at pH 5.6 were counted. Bacterial presence in the samples was detected by the turbidity developed in the aqueous phase of vials at pH 7.2 [7].

Total number of molds in the fuel was determined using membrane filtration technique as described by Fass and Miller [8].

2.7. Determination of biocide concentration in Diesel fuels:

The biocide was extracted from 600 ml Diesel fuel samples, (unknown Diesel fuel samples and control Diesel fuel sample containing 200 ppm biocide), into 30 ml of sterilized distilled water through vigorous mixing by magnetic stirrer for 120 minutes. The Diesel fuel and the aqueous phases were separated by centrifugation. The separated aqueous phase was diluted 1:3 with TSB medium. Aliquot of the diluted extract, successively decreased by 5%, were added into 20 ml sterilized test tubes. The volume in the first tube was 4 ml and volumes in all other test tubes was replenished to 4 ml by sterile TSB medium. All test tubes were inoculated with 0.1 ml ,(OD_{600} = 0.2), of pigment producing bacterium *Pseudomonas aeruginosa*. The test tubes were incubated for 20h at 30°C. The end point was determined as the highest dilution in which green color was not developed.

The concentration of the biocide in the unknown Diesel fuel samples were calculated as described in the following equation:

$$B=200 x D_1/D_2$$

B (ppm) - Biocide concentration in the unknown sample.

D_1 - End point dilution factor of control sample.

D_2 - End point dilution factor of unknown sample.

2.8. Chemical analysis of Diesel fuel samples:

Chemical analyses were performed in a reference fuel laboratory ("Technion", Haifa, Israel). The list of tests were presented in Table 1. The array of the tests is based on the Israel Defense Forces specifications [9].

3. RESULTS AND DISCUSSION

Stored Diesel fuels were routinely analyzed twice a year. Water or microbial sludge were not detected in samples taken from all three tanks during the five years period. Hydrocarbon utilizing bacteria were not detected in fuel samples during the experiment period. It could be explained by bacterial low resistance to fuel in comparison with mold spores [10]. Results of molds contamination and chemical analyses in LSRDF samples were summarized in the following.

3.1. **Untreated LSRDF 1:**

Fuel mold contamination levels (FCL) in upper layers and 'bottom-bottom' layers during the five years experiment were summarized in Figure 1. High FCL were detected in all the 'bottom-bottom' layer samples. Contrary to that, the FCL of upper layers, were high at the first year but decreased during the following four years. The decrease in mold contamination in the upper level might be explained by a slow settling of the mold spores during storage [8]. The LSRDF 1 chemical properties remained unchanged during all the five years storage period (Table 1).

3.2. **Biocide treated LSRDF 2:**

Fuel mold contamination levels and biocide concentration in the fuel samples during five years of storage were summarized in Figure 2. The results indicated that FCL in both upper and 'bottom-bottom' layers were markedly decreased following the biocide addition. FCL remained low during the five years of storage. The biocide concentration after five years storage was 100 ppm (out of 200 ppm introduced). The Diesel fuel biocide concentration, at the end of the fifth year, was sufficient to hinder microbial growth in occasional water phase. The standard chemical properties of the fuel remained unchanged throughout the experiment period (Table 1). However, the green dye marker was gradually diminished during the first year and simultaneously a heavy 'acidic' odor was developed in the fuel. This phenomenon was considered as early sign for fuel instability and was attributed to the presence of the biocide in the system.

3.3. **Stabilizer additive and biocide treated LSRDF 3:**

Fuel mold contamination levels and biocide concentration in fuel samples during five years of storage were summarized in Figure 3. FCL in both upper and 'bottom-bottom' layers were markedly decreased following the biocide addition and remained low throughout the five years experiment. The fuel biocide concentration decreased to half the initial concentration shortly after dosing and continued to decrease in a slow rate in the following four years. At the end of the fifth year it was 50 ppm (out of 200 ppm introduced). The marked decrease in biocide activity, during the first few months of storage, can not be attributed to the presence of water in the system since water could not be detected. A possible explanation might involve a "biocide-stabilizer additive" incompatibility which is usually the case in stabilizers-biocides packages.

Nevertheless, the biocide concentration in the fuel was sufficient to hinder microbial growth in occasional water phases. The Diesel fuel remained chemically unchanged throughout the five years storage (Table 1) and no "informal" deterioration could be observed.

The results indicated that untreated LSRDF can be stored for five years in precleaned, 50,000L, steel, underground storage tanks with no chemical deterioration. However, the high 'bottom-bottom' FCL developed, could be considered as a risk to the end user operability, especially when fuel distribution systems with no filtration or floating arms devices were involved. The addition of the tested biocide alone reduced the microbial contamination to below significant level but effected the fuel stability. It was evident that in the tested storage system only the combination of the stabilizer additive and biocide could assure a safe five years storage of LSRDF.

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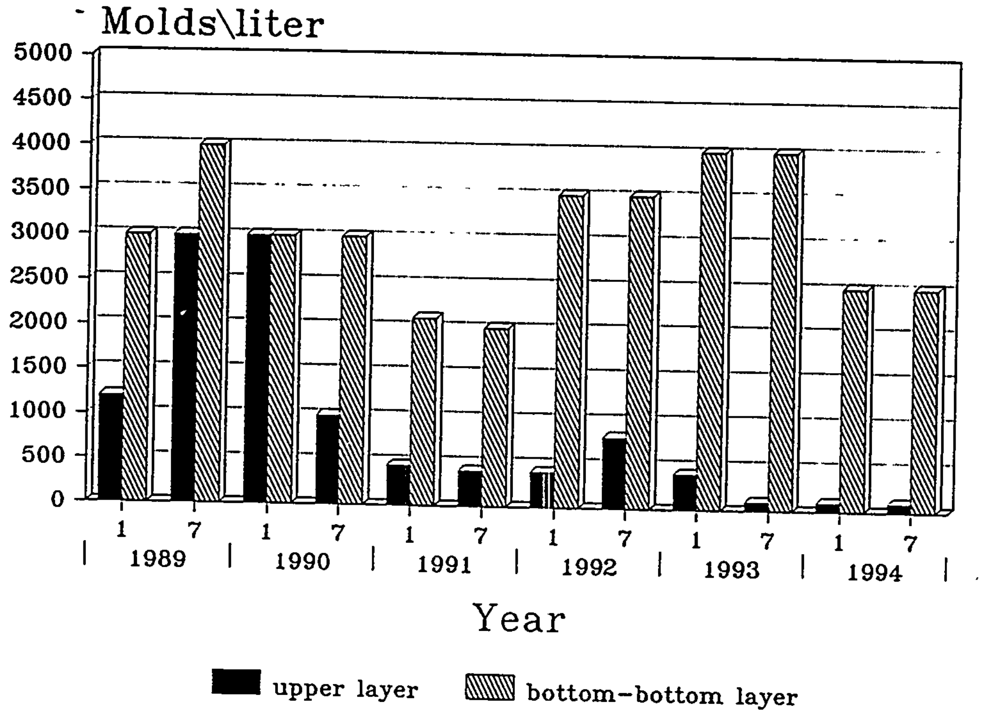

Figure 1: Molds count in stored Light Straight Run Diesel Fuel without additives (LSRDF 1). The fuel was stored for five years in 50,000L, steel, cylindrical, underground storage tank.

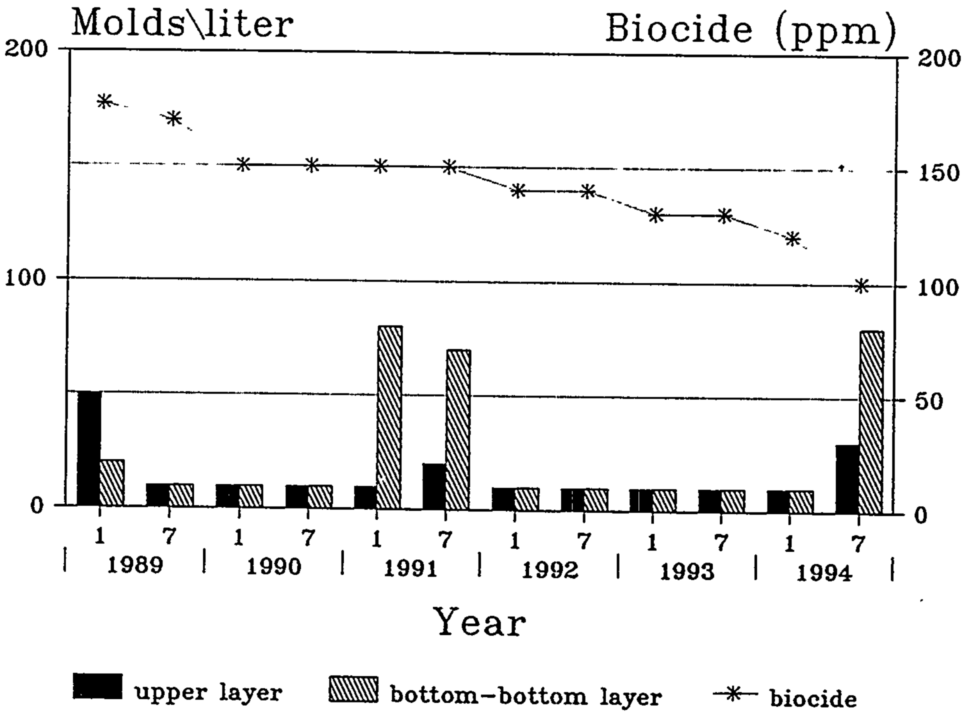

Figure 2: Molds count and biocide concentration in stored Light Straight Run Diesel Fuel with biocide (initial concentration was 200 ppm) (LSRDF 2). The fuel was stored for five years in 50,000L, steel, cylindrical, underground storage tank.

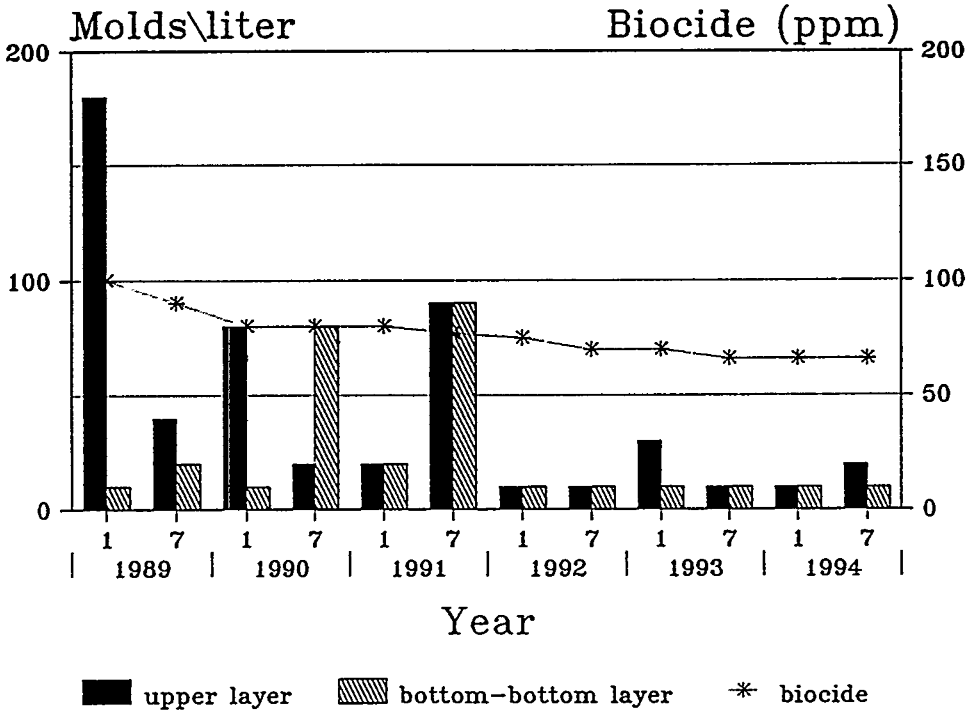

Figure 3: Molds count in stored Light Straight Run Diesel Fuel with stabilizer additives package (biocide and stabilizer additive initial concentrations were 200 ppm and 100 ppm respectively) (LSRDF 3). The fuel was stored for five years in 50,000L, steel, cylindrical, underground tank.

Table 1: Chemical analysis of LSRDF (at time 0 and after five years) stored in 50,000L, steel, cylindrical, underground storage tanks.

Characteristics	Test Method		LSRDF 1 years		LSRDF 2 years		LSRDF 3 years	
	IP	ASTM	0	5	0	5	0	5
Appearance			bright/clear	bright/clear	bright/clear	bright/clear	bright/clear	bright/clear
color (Visual)			green	green	green	light brown	green	green
Specific gravity (15^{o}C)	160	D-1298	0.841	0.843	0.843	0.841	0.843	0.843
Kinematic viscosity CST,40^{o}C	71	D-445	3.0	3.0	3.0	2.9	3.0	3.1
Ash content (%)	4	D-482	>0.01	>0.01	>0.01	>0.01	>0.01	>0.01
Water and sediments (%)		D-2709	>0.005	>0.005	>0.005	>0.005	>0.005	>0.005
Pour point, max. (^{o}C)	15	D-97	-15	-15	-15	-15	-15	-15
Cloud point, max. (^{o}C)	219	D-2500	-13	-13	-14	-14	-14	-14
Bromine No.			1.4	1.9	1.4	1.8	1.4	1.9
Total l acidity (mg KOH/gr)	177	D-664	0.06	0.05	0.06	0.09	0.06	0.09
Copper corrosion	154	D-130	1A	1A	1A	1A	1A	1A
Accelerated oxidation (mg/100ml)		D-2274	1.2	0.8	2.0	1.3	0.8	0.5
Carbon residue (10% bottoms,max)	14	D-524	0.06	0.1	0.12	0.09	0.13	0.11
Flash point (^{o}C)	34	D-93	80	84	84	80	84	84
Distillation:	123	D-86						
IBP (^{o}C)			193	198	190	182	197	199
10% of			235	233	234	228	238	240
50% of			272	270	271	271	273	275
90% of			309	306	307	309	308	308
EP (^{o}C)			333	323	331	332	332	333
Residue (%)			0.4	1.0	0.4	0.4	0.7	0.4
Total sulfur (%)	61	D-129	0.38	0.38	0.38	0.36	0.38	0.39
Diesel index	21		55	56	56	56	56	57

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STORAGE STABILITY OF LIGHT CYCLE OIL : STUDIES FOR THE ROOT SUBSTANCE OF INSOLUBLE SEDIMENT FORMATION

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Abstract

The storage stabilities of a raw and pretreated light cycle oils (LCOs) have been studied under the condition of ASTM D2274-88. The raw LCO was pretreated by five methods ; 10% sulfuric acid-extraction, 10% sodium hydroxide-extraction, methanol-extraction, active clay-treatment, and catalytic hydrotreating. The raw and pretreated LCOs were aged at 95°C for 144 hours while oxygen was bubbled. The pretreatment except 10% sulfuric acid-extraction showed the decreasing sediments. After removing the sediments by filtration, the changes of component of the residual oils before and after aging, were analyzed by GC/MS, GC/AED and GC/NPD. Remarkable changes were observed in nitrogen compounds such as anilines and indoles, sulfur compounds such as thiophenols, and oxygen compounds such as phenol and its derivatives. It was clarified that the sediment formation was caused by the mutual interactions among heteroatom-containing compounds mentioned above. In addition, unstable hydrocarbons were suggested to behave as key-compounds for sediment formation.

Introduction

In recent years, the main demand for oil products in Japan has changed from fuel oil to transportation fuel such as gasoline and diesel oil. Diesel oil has been produced mainly from straight run distillate. At present, the effective use of cracked gas oil such as LCO is becoming an important subject for oil industry with the increase of the demand of diesel oil.

Using a LCO as a blendstock of diesel fuel, one of problems is sediment formation because of its poor storage stability. As for the mechanism of insoluble sediment formation from LCO, many studies show that nitrogen compounds such as indoles, sulfur compounds such as thiols, and oxygen compounds such as phenols participate in the insoluble sediment formation1)~7). However, the mechanism of insoluble sediment formation is not still made clear in detail.

Unstable hydrocarbons which were easy to be oxidized, basic compounds, acidic compounds and polar compounds were considered as the root substances of insoluble sediment formation. The storage stability of LCO produced in Japan have been studied in order to get foundation data for establishment of improvement technology of storage stability and the evaluation method.

Experimental

Two fresh LCOs (LCO1 and LCO2) of which properties were shown in Table 1, were used as the sample oils. Hydrocarbons, sulfur compounds and nitrogen compounds were analyzed by GC/MS, GC/AED and GC/NPD.

LCO1 and LCO2 were filtered with membrane filter (pore size 0.8 μm) before using for the experiment. The LCO2 was pretreated as follows.

Acid treatment : Extracted two times in 50 ml of 10 % sulfuric acid from 500 ml of the sample oil, and washed the LCO with distilled water, and removed water.

Base treatment : Extracted two times in 50 ml of 10 % sodium hydroxide solution from 500 ml of the sample oil, and washed the LCO with distilled water, and removed water.

Methanol treatment : Extracted two times in 50 ml of methanol from 500 ml of the sample oil, and washed the LCO with distilled water, and removed water.

Activated clay treatment : Treated with 20 g of activated clay for 500 ml of the sample oil.

Hydrotreating : Hydrotreated the sample oil under three conditions shown in Table 2.

These sample oils were aged for 144 hours at 95 °C while oxygen was bubbled referring to ASTM D2274-88. After aging, the sample oils were filtered, and the amounts of sediment were measured.

The gas chromatographs, used for identification of components removed by each treatment of methanol, acid, base and activated clay and analyses of the components of the sample oils, were equipped with capillary column of methylsilicone (length 25 m, I.D. 0.32 mm, film thickness 0.17 μm). The oven temperature program was from 50 °C to 300 °C at 8° C/min.

The insoluble sediments obtained after aging were analyzed by an elemental analyzer.

Results and Discussion

Amounts of the sediment

The amounts of the insoluble sediments formed after aging are shown in Table 3. As for the LCO2, the largest amount of insoluble sediment was obtained from raw oil. The amount of sediment of acid treatment oil was comparable to that of raw oil. The amounts of insoluble sediments of methanol treatment oil and activated clay treatment oil corresponded to from 1/4 to 1/3 of that of raw oil. In base treatment oil, the amount of insoluble sediment was small, and it was ca.1/7 of that of raw oil. The most effective treatment on decreasing the insoluble sediment was hydrotreating, and hydrotreating oils, (H1) and (H3), gave the insoluble sediments less than 1/10 of that of raw oil.

Compositional change of LCO1 by aging

The LCO1 was divided into four fractions by silicagel column chromatography and the hydrocarbons in each fraction were analyzed by GC/MS and GC/AED. As a result, normal or branched paraffins from C 10 to C 24 ,alkylbenzenes (C1 ～ C6) and polycondensed compounds such as indanes, naphthalenes and phenanthrenes were detected. The concentrations of these hydrocarbons did not change so much by aging.

As for sulfur compounds, benzothiophenes and dibenzothiophenes were detected as major components by the GC/AED analysis, but obvious change was not recognized in their concentrations by aging.

As for nitrogen compounds, anilines, indoles and carbazoles were detected by the GC/NPD analysis. The amounts of anilines and indoles decreased remarkably by aging (Figure 1).

Components removed by each treatment

The major components of sulfuric acid extract were basic nitrogen compounds such as anilines and phenylaminobenzenes, however carbazoles were not contained in extract at all (Figure 2). The major components of sodium hydroxide extract were alkylphenols from C1 to C4, and small amounts of indanols, naphthols, and phenylphenols were also contained. A very small amount of thiophenols was recognized (Figure 3).

The GC/MS analysis of the methanol extract showed that polycondensed aromatic compounds were major components of the extract, and that sulfur compounds were difficult to be extracted by methanol, and that a small amount of benzothiophenes was extracted. As for nitrogen compounds, indoles and carbazoles were extracted more selectively by methanol than anilines.

The major components removed by activated clay treatment were polycondensed aromatic compounds similar to the methanol extract. Normal paraffins were contained in addition to those. Selectivity in extraction for hydrocarbons of activated clay treatment was inferior to methanol treatment. As for sulfur compounds and nitrogen compounds, a tendency was similar to the methanol treatment (Figure 4).

Above-mentioned results were summarized in Table 4.

Compositional change of sample oil by each treatment

Considering the components removed by each treatment, sample oils were analyzed mainly on sulfur compounds, nitrogen compounds and oxygen compounds.

The sulfur compounds in each sample oil were classified into benzothiophenes, dibenzothiophenes, thiophenols, and the others (shown to Table 5). From Table 5, it was recognized that thiophenols in sample oil decreased remarkably by base treatment, methanol treatment, and activated clay treatment. The amount of thiophenols decreased greatly even though those of benzothiophenes and dibenzothiophenes did not change by aging. Many acidic compounds containing sulfur atoms were detected in the higher boiling range of gaschromatogram of acidic extract of aged sample oil. These compounds were considered to be formed during the aging process even though their structures have not been identified.

The nitrogen compounds in each sample oil were classified into anilines + indoles, carbazoles, and the others (shown in Table 5). Though basic nitrogen compounds such as anilines were contained in the sulfuric acid extract, considerable amounts of basic nitrogen compounds still remained in acid treatment oil. It may be considered that the amount of sulfuric acid used for the treatment was not enough. In base treatment oil, there appeared no changes in the concentrations of basic nitrogen compounds, whereas the concentrations of neutral nitrogen compounds such as carbazole were observed to decrease to some extent. In methanol treatment oil and activated clay treatment oil, the amounts of indoles and carbazoles decreased. As for hydrotreating oils, (H1) and (H2) of which treating temperatures were lower showed little changes in the concentrations and compositions of nitrogen compounds. On the other hand, (H3) of higher temperature treatment showed that the concentrations of anilines decreased remarkably in nitrogen compounds.

The oxygen-containing acidic components are summarized into two groups, phnols and others. The former consists of alkylphenols, indanols, naphthols, and phenylphenols. The amounts of these groups in each sample oil are shown in Table 5. In base treatment oil, the amount of phenols decreased remarkably. In methanol treatment oils and activated clay treatment oil, phenols decreased to 1/3 in quantity. Very little differences were observed in the total amounts of phenols between before and after aging sample oils. However, detailed analysis of GC/AED indicated that some phenols decreased in quantity and that some new peaks appeared in the higher boiling range of gaschromatogram of aging oil(Figure 5). It is thought that some new compounds were formed by oxidation of hydrocarbons in sample oil, and changed to acidic components.

It was suggested that unstable hydrocarbons participated in the insoluble sediment formation greatly, because hydrotreating, including in case of lower treating temperatures, was effective to the depress of sediment formation. The structures of the unstable hydrocarbons are now under investigating.

Methanol-extractable/hexane-insoluble solids (MEHI), which was reported to participate in the sediment formation greatly5), was measured in each sample oil. In our sample oils the amounts of MEHI were shown to be very small.

Elemental analysis of insoluble sediments

Elemental analysis data of insoluble sediments formed from aging sample oils are shown in Table 6. This table shows that the concentrations of carbon, hydrogen, sulfur, and oxygen of sediment from acid treatment oil are similar to those of raw oil. However, The nitrogen content of sediment from acid treatment oil is lower. Table 6 also shows that insoluble sediments from methanol treatment oil and activated clay treatment oil include of lower contents of sulfur and oxygen and higher contents of nitrogen than the sediments from the two oils mentioned above. The sediments were formed in too small amount to analyze from base treatment oil and hydrotreating oils.

The participations of sulfur compounds, nitrogen compounds, unstable hydrocarbons, and oxygen compounds to the insoluble sediment formation were considered from the results mentioned above.

(1) Sulfur compounds

Thiophenols were detected in the removed components of the base treatment that might be effective on the depress of insoluble sediment formation. The larger amount of thiophenols were contained in sample oil, the larger amount of insoluble sediment was formed. Thiophenols decreased obviously by aging sample oil. Sediments produced in high yield possessed sulfur atoms in high content. It is suggested that the sulfur compounds such as thiophenols can be one of the root substances for sediment formation.

(2) Nitrogen compounds

Very small amounts of sediments were formed from the base treatment oil and hydrotreating oils even though the nitrogen concentrations of these oils were rather higher. These data suggest that nitrogen compounds are not direct root substances for sediment formation, they seemed to rather behave as oxidation inhibitors. It was also shown that sediments produced in lower yield possessed to nitrogen atoms in higher content, which indicates that some nitrogen compounds are easily polymerized and caught into the sediment.

(3) Unstable hydrocarbons

At beginning stage of this research, unsaturated compounds such as olefins and indenes were considered as unstable hydrocarbons above mentioned. The data of hydrotrearing oils seem to support this consideration. However, any differences have been observed between compositions of such compounds before and after aging.

(4) Oxygen compounds

Phenols are major components of oxygen compounds and easily removed by base treatment. This treatment showed remarkable effect on decreasing sediment formation, although the difference between the composition of phenols before and after aging was small. Above data and the similarity of properties between phenols and thiophenols suggest the possibilities that phenols participates in sediment formation in some ways. In order to clarify these problems, accumulation of stability data of many types of oils, including the data of individual molecule, are required.

Conclusions

To summarize the results above mentioned, in oxidation deterioration of LCO, the unstable hydrocarbons which are easy to be oxidized are oxidized in the first place, but they do not proceed to insoluble sediment by themselves. If sulfur compounds such as thiophenols (and/or phenols) exist here, sediment is formed. On the other hand, nitrogen compounds repress the oxidation of hydrocarbons which follows to the repress of sediment formation. They are oxidized and taken into sediment by themselves. In order to make this consideration more certain, further studies will be necessary about sulfur compounds, unstable hydrocarbons and phenols. In particular, the establishment of fine analytical technique about individual component of fuel oil are required.

Acknowledgments

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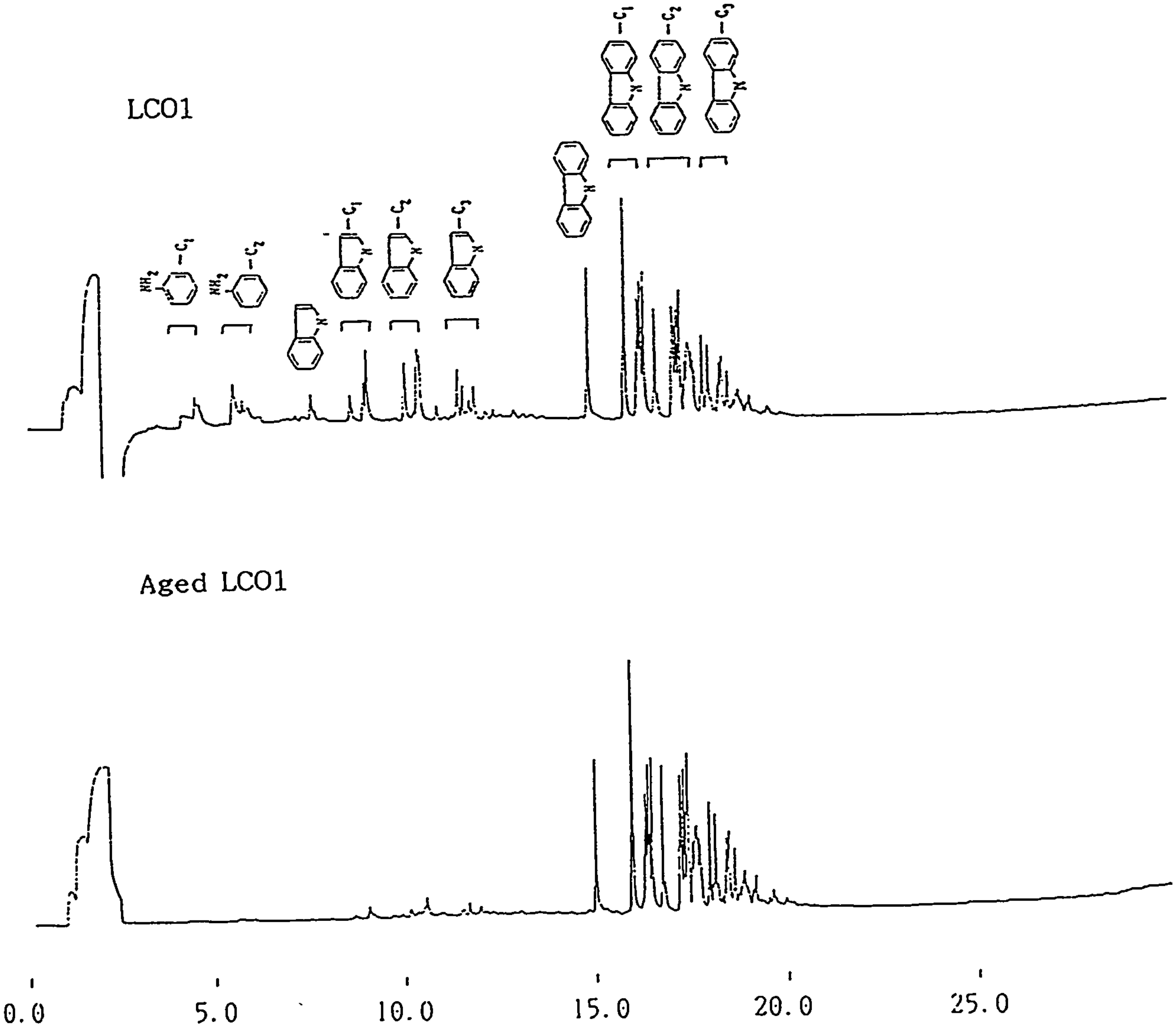

Figure 1. NPD gas chromatograms of LCO1 and aged LCO1.

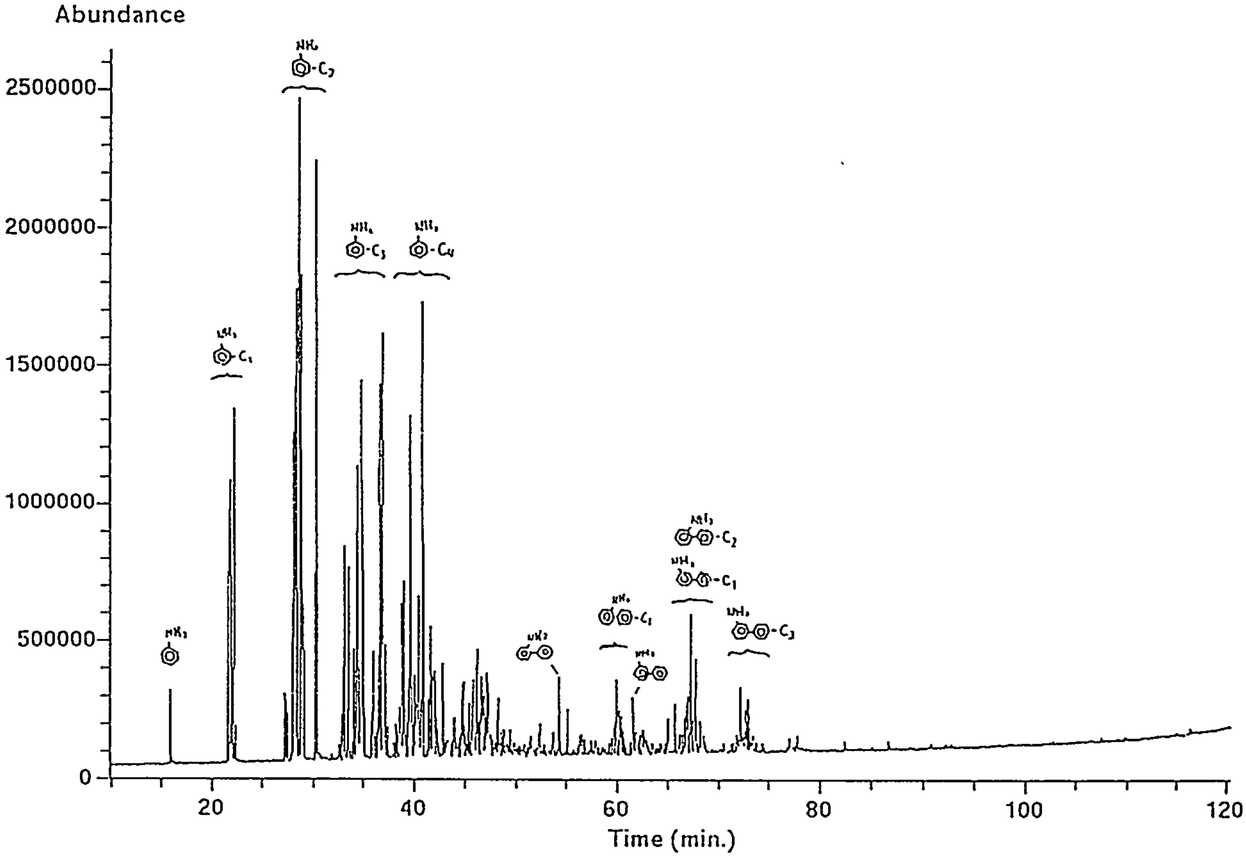

Figure 2. Total ion chromatograms of removed components by 10%H_2SO_4 treatment.

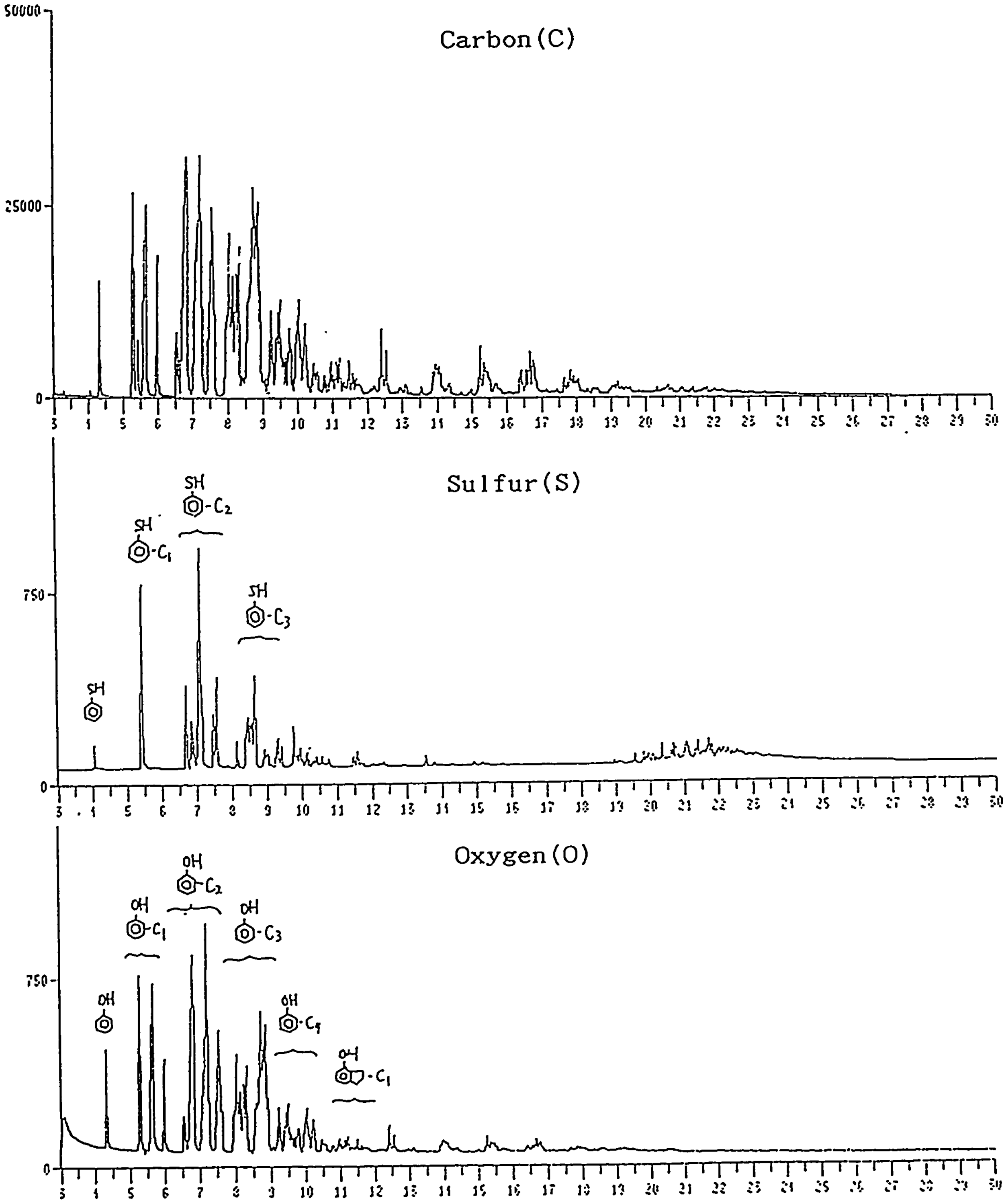

Figure 3. AED(C,S,O) gas chromatograms of removed components by 10%NaOH treatment

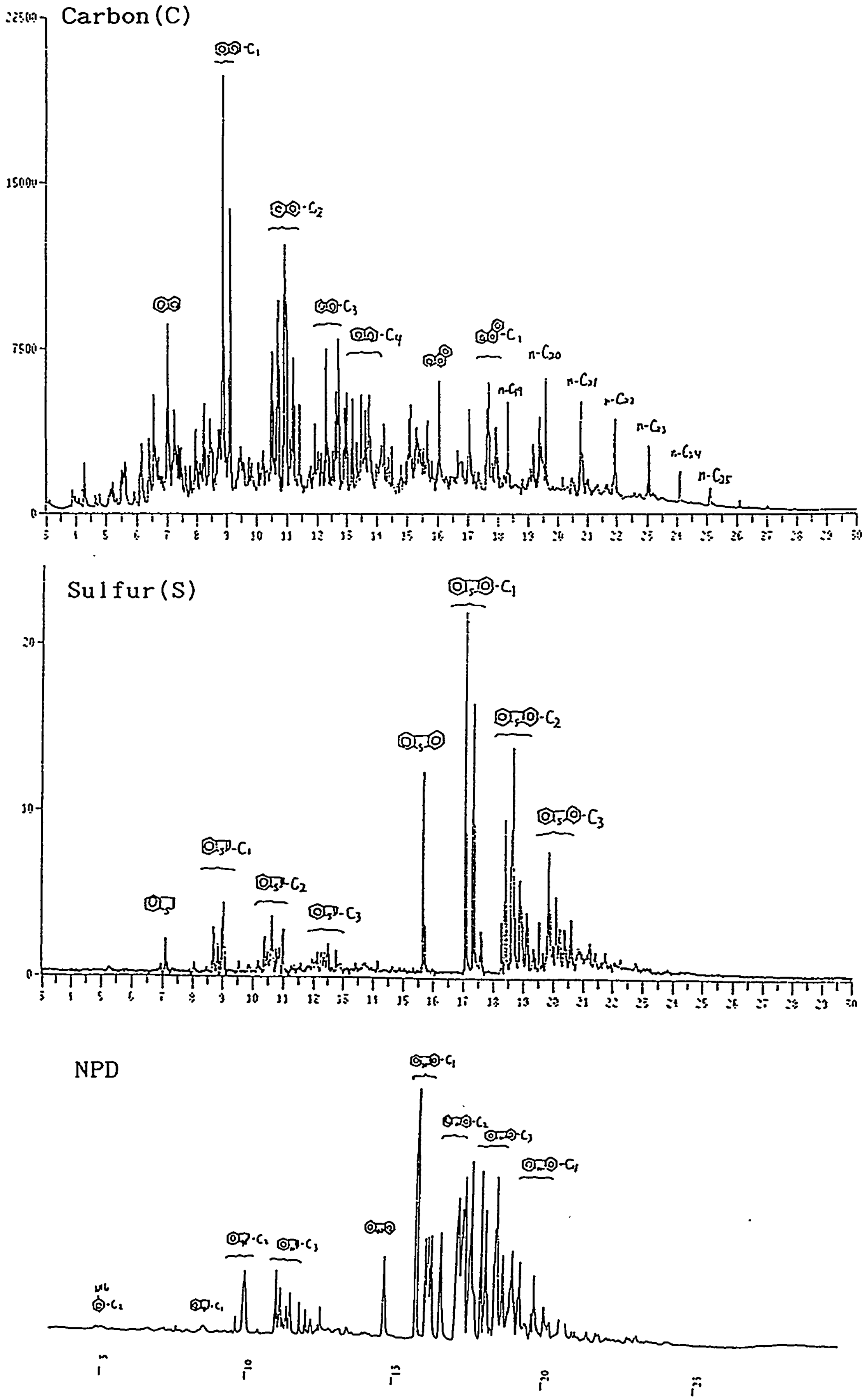

Figure 4. AED(C,S) and NPD gas chromatograms of removed components by activated clay treatment.

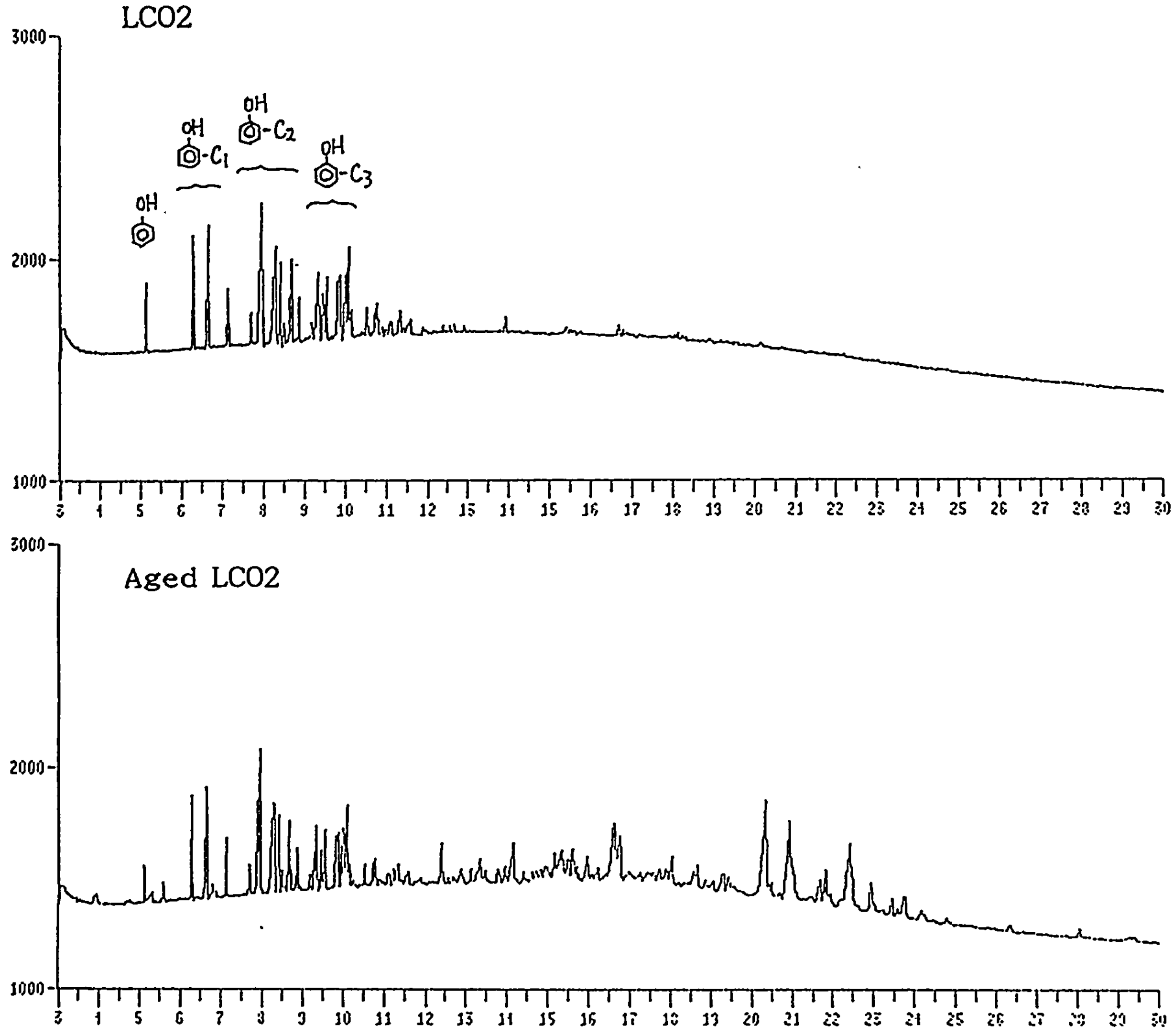

Figure 5. NPD gas chromatograms of acidic extract of LCO2 and aged LCO2.

Table 1. Properties of sample LCO.

LCO	Density (g/cm^3)	Total S (wt%)	Total N (ppm)	Basic N (ppm)	Saturates (vol%)	Olefins (vol%)	Aromatics (vol%)	Distillation (°C) 10%	50%	90%
1	0.8812	0.07	73	15	37	4	59	196.0	242.5	307.5
2	0.9110	0.10	120	19	33	2	65	221.5	266.0	336.0

Table 2. Conditions of hydrotreating.

Treating No.	LHSV	Hydrogen Pressure (atm)	Catalysts	Reaction Temp. (°C)
1	20	10	$Pt/Al_2.O_3$	225
2	10	30	$Ni\text{-}Mo/ Al_2.O_3$	200
3	10	30	$Ni\text{-}Mo/ Al_2.O_3$	300

Table 3. Comparison of insoluble sediment production. Sample oils were pre-filtered and aged for 144 hours at 95°C while oxygen was bubbled. Then samples were filtered and the insoluble sediments were weighed.

Sample	Insoluble sediment (mg/100ml)
LCO1	4.0
LCO2	17.6
Acid treatment LCO2	13.6
Base treatment LCO2	2.3
Methanol treatment LCO2	5.6
Activated clay treatment LCO2	3.5
Hydrotreating LCO2 (H1)	1.5
Hydrotreating LCO2 (H2)	2.6
Hydrotreating LCO2 (H3)	1.0

Table 4. Removed components by each treatment. Extracts of acid, base, methanol and activated clay were analyzed by GC/MS, GC/AED and GC/NPD.

Treatment	Sediment (mg/100ml)	Hydrocarbons	S-compounds	N-compounds	O-compounds
Acid	13.6	n.d.*	n.d.	anilines phenylaminobenzens	n.d.
Base	2.3	(trace)	thiophenols	n.d.	phenols
Methanol	5.6	naphthalenes phenanthrenes indanes, etc	thiophenols benzothiophenes	indoles carbazoles anilines	phenols
Activated clay	3.5	naphthalenes phenanthrenes indanes, etc.	thiophenols benzothiophenes	indoles carbazoles anilines	phenols

* None detected.

Table 5. Contents of S-compounds, N-compounds and O-compounds in samples. S-compounds and O-compounds in sample oils were determined by GC/AED. N-compounds in samples were determined by GC/NPD.

Sample	S-compounds (wt%S)				N-compounds (wt%N)			O-compounds (wt%O)	
	BT*	DBT**	thiophenols	total-S	anilines,indoles	carbazoles	total-N	phenols	others
LCO2	0.024	0.052	0.000030	0.097	0.0064	0.020	0.027	0.00062	0.00001
Acid	0.019	0.052	0.000024	0.097	0.0055	0.018	0.023	0.00050	<0.00001
Base	0.018	0.052	<0.000001	0.094	0.0064	0.019	0.025	0.00001	<0.00001
Methanol	0.017	0.051	0.000009	0.089	0.0059	0.015	0.021	0.00025	<0.00001
A.Clay	0.017	0.050	0.000003	0.086	0.0036	0.016	0.019	0.00023	<0.00001
Aged LCO2	-	-	0.000001	-	-	-	-	0.00062	0.00055

* benzothiophenes, ** dibenzothiophenes

Table 6. Elemental analyses of insoluble sediments. Insoluble sediments except for base treatment and hydrotreating were analyzed by CHNS elemental analyzer.

Sample	%C	%H	%S	%N	%O*
LCO1	74.5	5.3	2.0	2.8	15.4
LCO2	77.8	5.1	1.3	3.2	12.6
Acid treated LCO2	79.5	5.1	1.3	2.7	11.4
Metanol treated LCO2	81.7	5.4	0.7	4.3	7.9
A.clay treated LCO2	84.4	5.4	0.5	5.1	4.6

* %O = 100 - (%C + %H + %S + %N)

5th International Conference on
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Rotterdam, the Netherlands
October 3-7, 1994

AUTOMATIC STABILITY ANALYZER OF HEAVY FUEL OILS

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INTRODUCTION

NESTE has a long history in development of production process and in the improvement of product quality by increasing automated quality adjustment and control. The objective has been to raise production efficiency and to ensure the maintenance of quality levels when using different crude oil grades, and to make economically such products that meet the requirements of the market.

STABILITY

Stability or storage life is an important quality parameter for heavy fuel oils. In the highly optimized oil refineries it is especially important to control the stability of the heavy fuel oils produced from thermal cracking units. The stability is influenced by the type and quantity of asphaltene particles in the oil. High production temperatures may cause some changes in quality.

AUTOMATIC STABILITY ANALYZER

Neste Scientific Services has developed an automatic on-line process analyzer both to meet the needs of production and product development laboratories.

OPERATION OF THE ANALYZER

The operation of the stability analyzer is based on the optic control of asphaltene content in heavy fuel. Oil samples are measured either directly from the process or from laboratory sample.

The computer-controlled process analyzer automatically takes a sample from desired process stream at regular time intervalls and out puts the stability figure in the process control room about every ten minutes. That is why this figure can be used as an important controlling parameter for quality in process control computer system of the thermal process. Depending on the process, the stability analyzer can be connected as a part to the control system in different thermal cracking units (Figure 1).

The on-line process analyzer (Fig.2) must be equipped with an explosion proof safety system with instrument air purge, if there is not a safe analyzer shelter available on the field. The oil sample line is linked to the analyzer from the production process through sample handling system.

From one to six oil samples of 10 gramms are weighed in the sample carousel of the lab scale stability analyzer (Fig.3). The analyzing result of each sample can be received in 5 to 10 minutes. The corresponding manual procedure takes several hours.

APPLICATION OF THE ANALYZER

The developed method for measuring stability can be used with heavy fuel oils produced from a wide variety of different crude oils.

The stability analyzer is most appropriate in heavy fuel oil production plants like thermal cracking units. In addition, oil quality control and product development laboratories can receive the stability figure quickly by using the stability analyzer.

Since most heavy fuel oils are blended from different refinery components or products, it is therefore important to measure the stability of the final product for the market (Fig. 4).

ADVANTAGES

The major benefit of the stability analyzer is based on both more precise cracking process control and saving of energy and saving in solvent when blending the final product to right viscosity value. The benefit is considerable and the pay back time of the analyzer investment is very short.

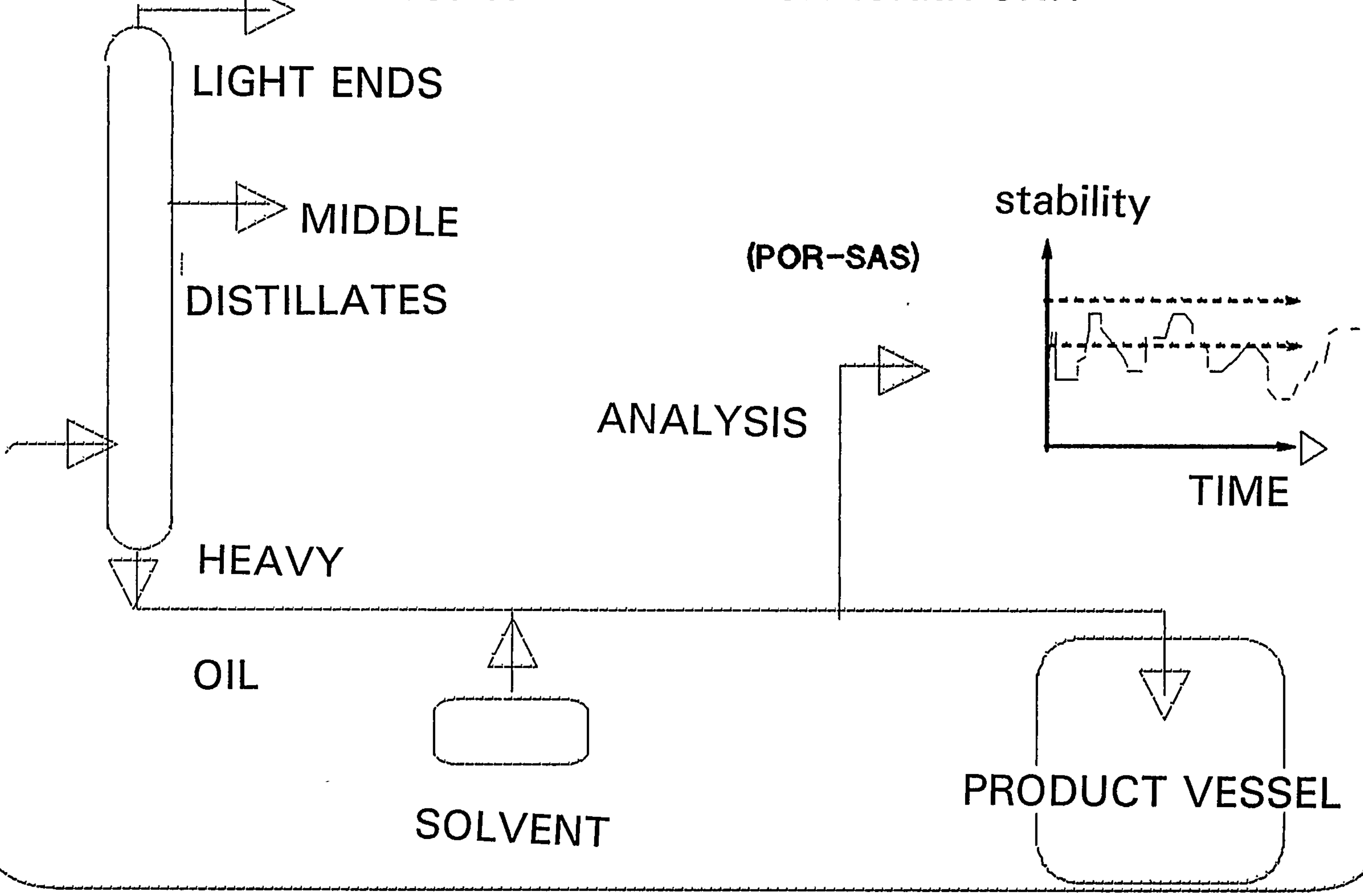
The on-line analyzer measures quickly and accurately all the changes and deviations in the process, which may occur while changing the feed oils in the process.

With the help of process analyzer the changes in production quality can be noticed shortly after they occur, and necessary correcting measures can be done to the process before producting large amounts of off-spec product (Fig.5).

NESTE SCIENTIFIC SERVICES

MIT2

FIG. 1: THERMAL CRACKER UNIT



LIGHT ENDS

MIDDLE DISTILLATES

HEAVY OIL

SOLVENT

ANALYSIS

(POR-SAS)

PRODUCT VESSEL

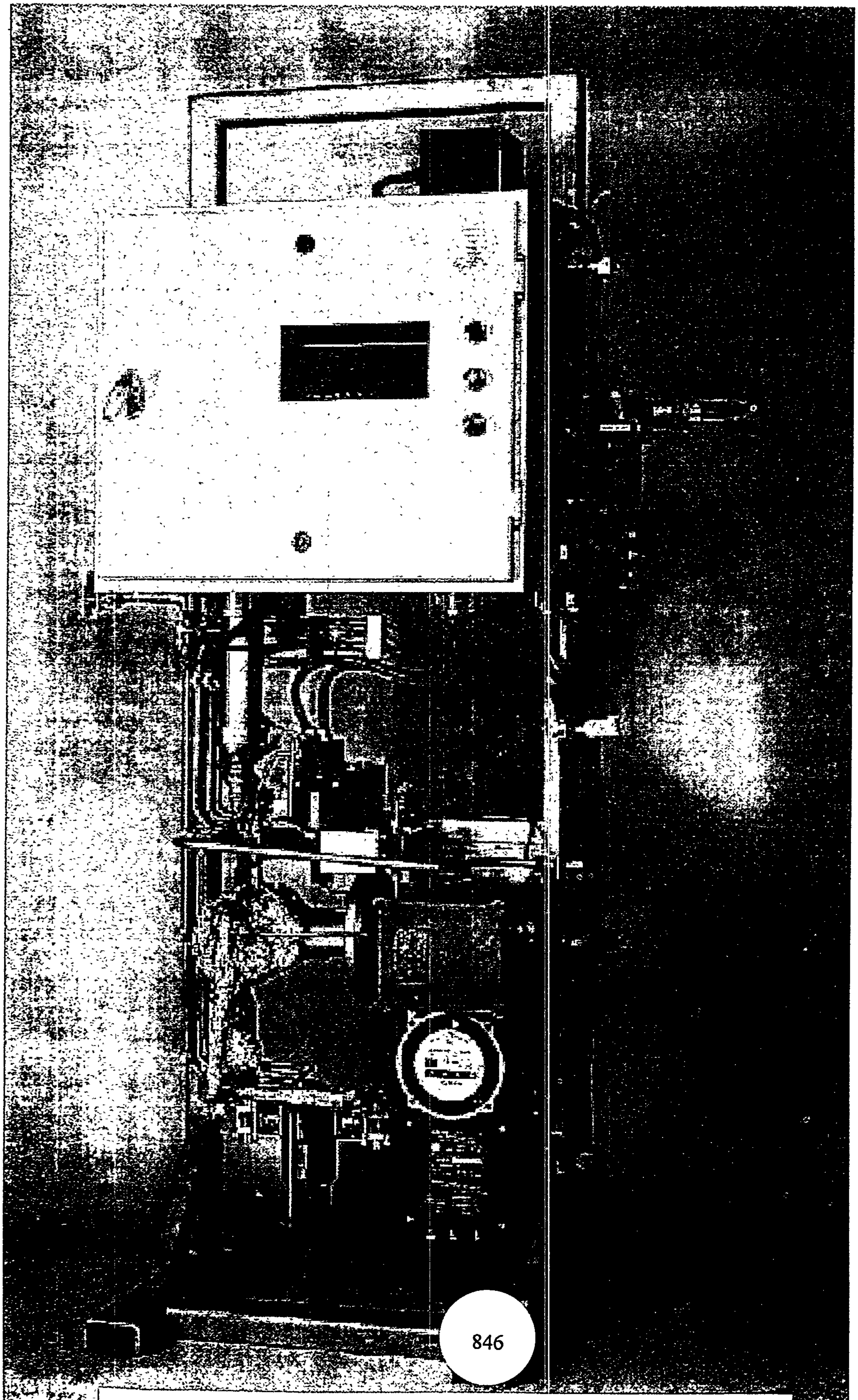


FIG.2: ON LINE STABILITY ANALYZER

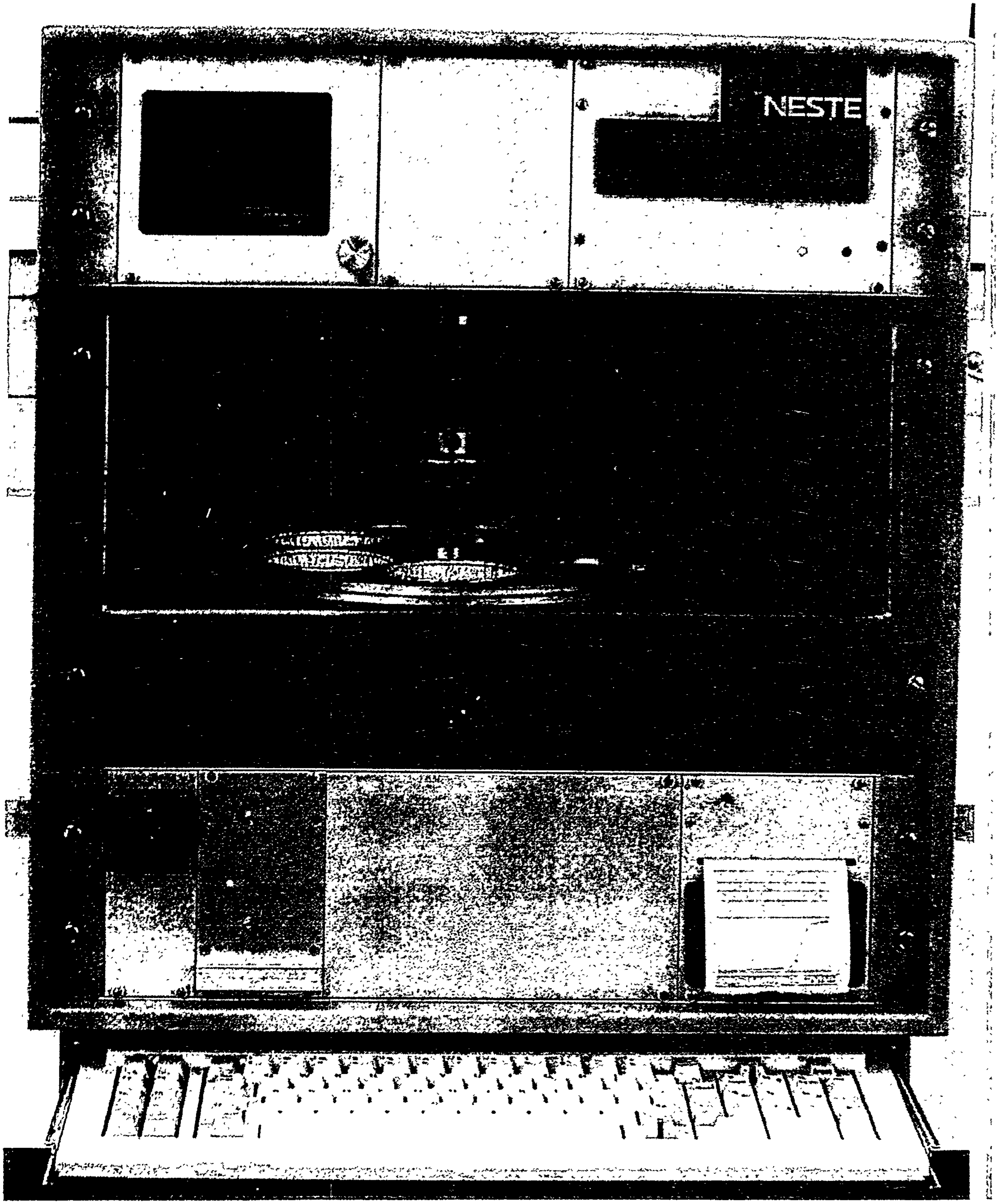


FIG.3: LABORATORY STABILITY ANALYZER

FIG.4: STABILITY OF HEAVY OIL IN THERMAL CRACKING PROCESS VERSUS TIME

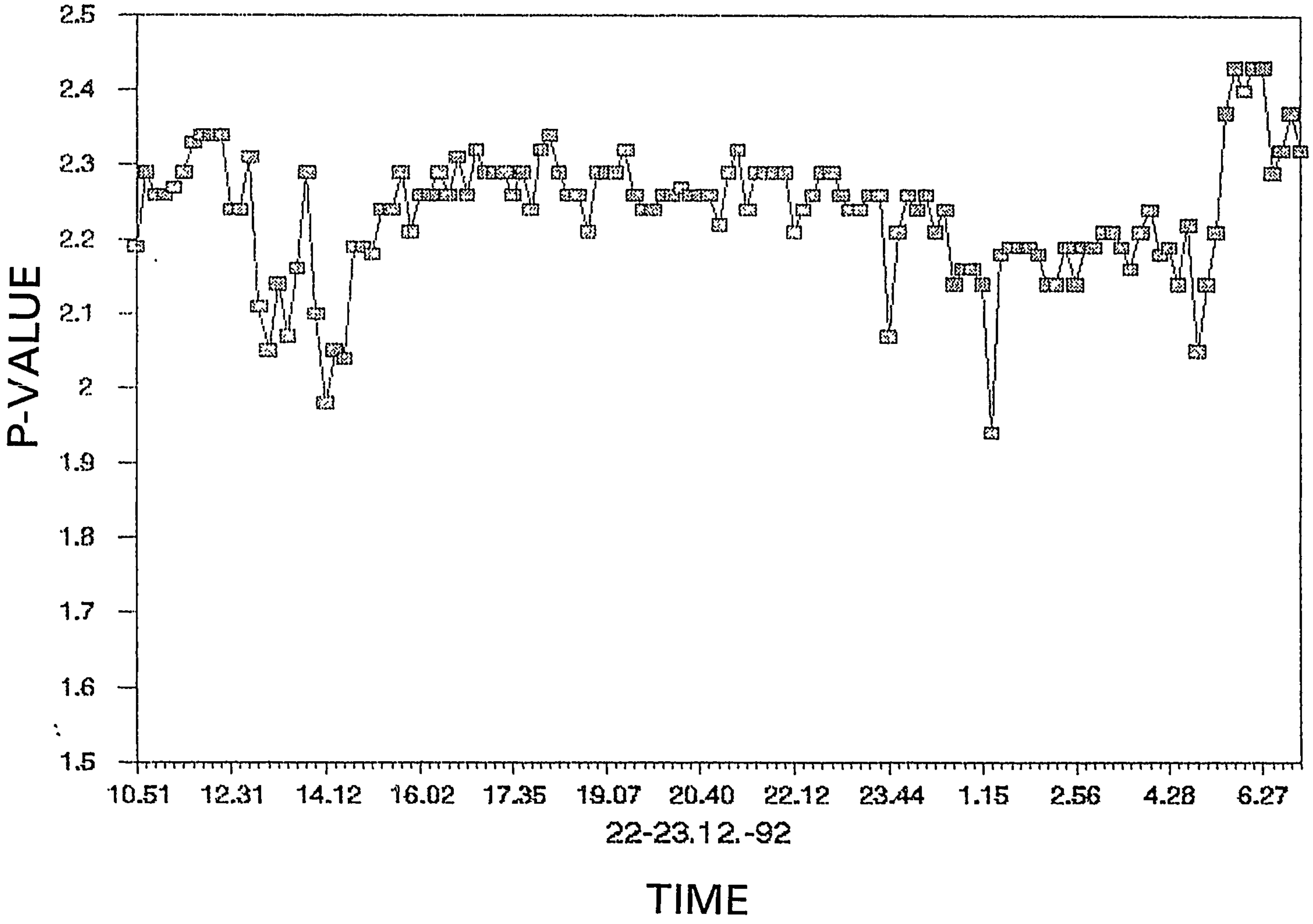
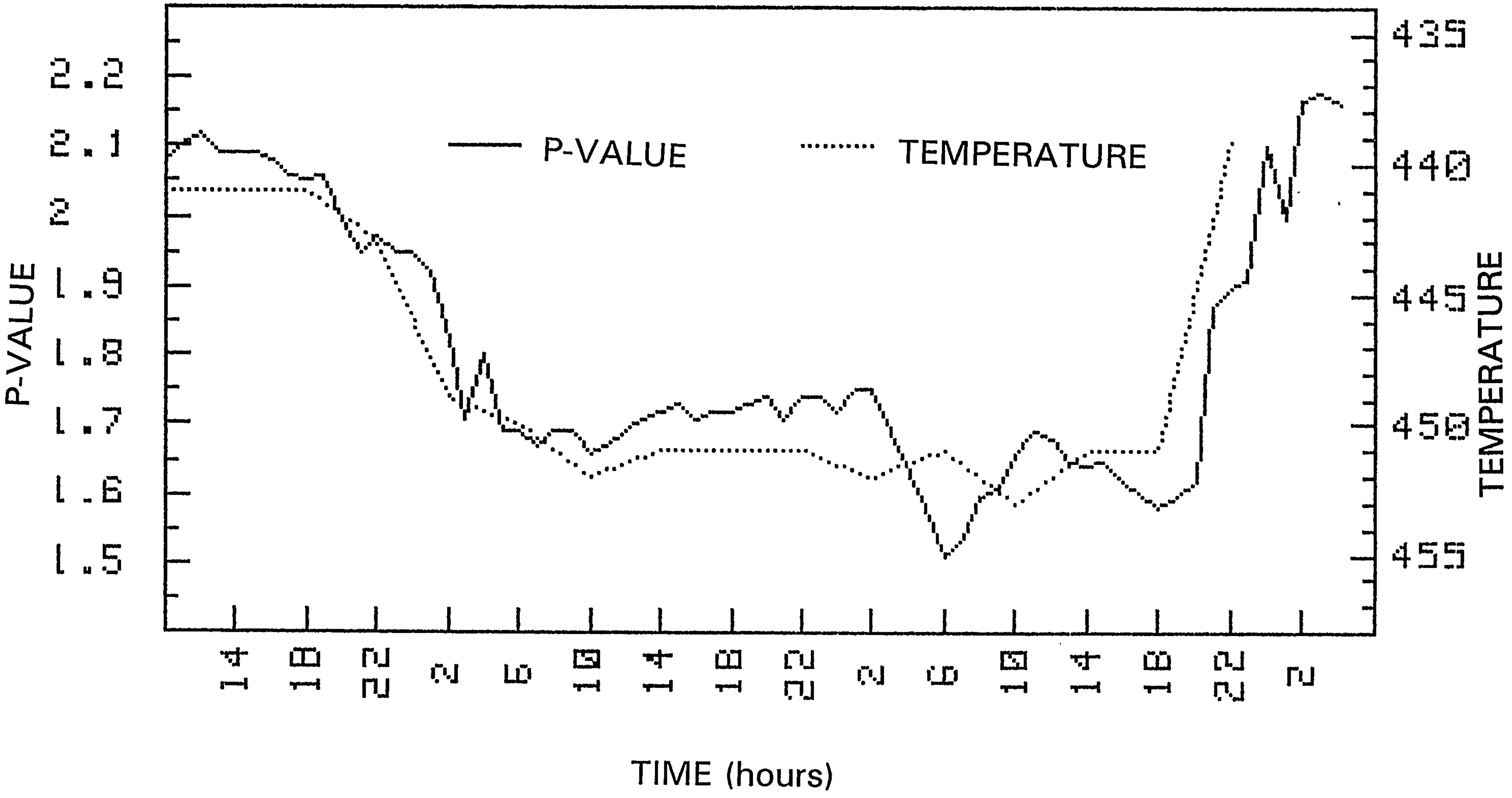


FIG.5: CORRELATION OF STABILITY AND TEMPERATURE IN THERMAL CRACKING PROCESS



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EFFECT OF COAL CONCENTRATION ON STABILITY OF DISTILLATE FRACTIONS FROM COPROCESSING

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ABSTRACT

Naphtha, light gas oil and heavy gas oil fractions obtained coprocessing 5 wt % and 30 wt % maf Forestburg subbituminous coal and Cold Lake vacuum bottoms were characterized for physical and chemical properties. These primary distillate fractions which were obtained in a non-catalytic process were stored at 43°C for up to 16 weeks in air to determine their storage stability before being processed to produce commercial synthetic crude oil. The initial results obtained from accelerated stability test (D2274) and total acid number (D974) predicted that the distillate fractions obtained using 30 wt % coal were less stable than the distillates obtained using 5 wt % coal. A 16-week aging test at 43°C confirmed the initial prediction. Very little or no filterable sediment was formed during 16 weeks in bottles containing low coal and high coal naphtha fractions. Sediment formation increased as the boiling point of the fraction increased and the coal concentration of the initial feedstock from which the distillates were obtained increased. The formation of adherent gum was more noticeable and increased substantially with time. Although more adherent gum is formed in high coal naphtha, considerably less adherent gum is formed in high coal light gas oil. The heavy gas oil fraction obtained in the high coal run produced more adherent gum than the corresponding fraction from low coal after 16 weeks. The initial existing gum in high coal naphtha was nearly double that of the low coal naphtha and increased slightly with time. Substantially more existing gum was found in high coal light gas oil than the low coal light gas oil and increased during the 16 week test. Overall, distillates from the high coal run produced more gum and the total gum (mg/100 mL) for all samples tested increased with time.

INTRODUCTION

Distillate fuels derived from tar sand, shale and coal may substitute straight run distillates as the demand for distillate fuels is increased. Syncrudes from these sources have been refined to produce fuels which have been shown in some cases to meet required specifications for petroleum-based fuels [1]. However, distillate fuels containing raw syncrude distillates are usually found to be less stable than straight run fuels. For instance, addition of light cycle oil (LCO) obtained from cracking of heavy fractions into automotive diesel fuel resulted in formation of insoluble particles and gum on storage of the fuel [2].

Synthetic fuels produced in coprocessing where a mixture of coal and heavy oil/bitumen is being simultanously upgraded contain both coal and bitumen-derived materials which may not only be stable but also incompatible [3].

The objectives of the present work reported here were to characterize primary CANMET coprocessing distillate fractions to determine the inherent stability of these products. Secondly, to study, what effects increasing coal concentration in the initial feedstocks from which these distillates are produced, will have on their properties and storage stabilities of these syncrude distillates.

EXPERIMENTAL

SAMPLE DESCRIPTIONS

Light and heavy ends products were selected from CANMET's coprocessing PDU for stability tests. Coprocessing experiment using 5 wt % maf coal is referred to in the text and tables as low coal and the experiment using 30 wt % maf coal is referred to as high coal. The products were distilled into naphtha (IBP-185°C), light gas oil (185-335°C), heavy gas oil (335-525°C) and residue (+525°C). The distillate fractions were then filtered using 102 mm Gelmen type A/E glass fibre filter papers into clean bottles and stored under nitrogen in a refrigerator. These samples are referred to in the text and tables as "initial" samples.

Aliquots of initial low and high coal naphthas, light gas oils and heavy gas oils were subjected to different analyses including oxidation stability (D525), copper corrosion (D130), total acid number (TAN, D974), existing gum (D381) density (D4052), viscosity (D445), aromaticity (^{13}C NMR using a Varian XL-300), Aniline point (D611), simulated distillation (D2887)and elemental analyses (C,H,O) by a CHN 240 Perkin Elmer analyzer, nitrogen (D4629) using a Dohrman analyzer and sulphur (D4294) using an X-ray analyzer (Gamma Tech Model 100). Accelerated stability test (D2274) was carried out on light gas oils only and hydrocarbon type (PONA) analysis was performed on naphtha and light gas oil fractions using a combination of GC/MS (HP 5890 GC and Finigan Incos-50 MS) and NMR (Varian XL-300). Metals (Ni,V,Fe) for heavy gas oil fractions were analyzed using a Perkin Elmer atomic absorption spectrometer model 5000.

STABILITY TESTS

For storage stability and determination of sediment and adherent gum a modified method by Brinkman and Bowden [4] was adopted in this work. Initial samples (200 mL) of low coal and high coal naphthas, light gas oils and heavy gas oils were transferred to bottles and stored at 43°C for up to 16 weeks. Storage stability tests were conducted in a Blue M explosion proof oven at 43±1°C.

Sufficient duplicate bottles containing naphtha and light gas oil fractions from low and high coal runs were placed in storage so that pairs of each sample could be removed after 4, 8, 12 and 16 weeks. Four empty bottles (one for each test period) were also placed in the oven to be used as blanks.

The duplicate aged filtrates of low and high coal naphtha and light gas oil fractions were analyzed for existing gum (D381), solvent washed gum and total acid number. For existing gum determinations, the naphtha fractions were treated at 162°C for 3 h and the light gas oil fractions at 210°C for 6 h. Other determined properties of the aged samples were density, viscosity, aromaticity, aniline point, elemental compositions, boiling point distributions, hydrocarbon type distributions (PONA) and metals analysis.

RESULTS AND DISCUSSIONS

Primary coprocessing products contain both coal and bitumen-derived liquids which require further processing to meet refinery specification as synthetic crude oil. Table 1 shows the comparison between the properties of the raw coprocessing distillates reported in this paper and commercial synthetic crude from tar sand [5]. It is clear that the raw coprocessing distillates contain higher sulphur, nitrogen and oxygen compared with SCO from Syncrude operation. Heteroatom containing molecules are known to participate in residue formation during storage. These problematic components can be removed by further processing to produce commercial synthetic crude. It is the objective of the present work to investigate the effect of composition of raw coprocessing distillates on residue formation before they are processed to produce commercial SCO.

PHYSICAL AND CHEMICAL PROPERTIES

The properties of unaged (initial) coprocessing distillate fractions are shown in Table 2. The oxidative stability test (D525) on all three fractions from both low and high coals showed no break point up to 45 h (2700 min). In comparison petroleum unleaded gasoline showed a break point (induction period) at 1440 min and a naphtha fraction obtained in the EDS coal liquefaction process of Illinois No. 6 showed a break point at 3180 min [4]. Significant evidence that untreated oils have a higher resistance to oxidation than hydrotreated oils [6]. It was suggested that sulphur and nitrogen compounds present as polar compounds in untreated oils inhibit oxidations [7-8]. It was shown later that an increase in saturated hydrocarbon content increases oxidative stability [9-10].

The copper corrosion (D130) rating of the naphtha from the low coal run was shown to be higher due to its higher sulphur content compared with that of the high coal naphtha. Higher boiling fractions exhibited a similar rating. The accelerated stability test (D2274) was carried out on the light gas oil fraction only. Relatively large amounts of residues were formed in both high and low coal light gas oils. The total acid number test (D974) indicated that all three fractions from the high coal concentration run have higher acid numbers than the corresponding fractions obtained in the low coal concentration run. Light gas oil fractions in both low coal and high coal runs contained a higher proportion of acidic components than the corresponding naphtha fractions. This may indicate a higher amount of coal-derived liquids incorporation into heavier distillates. Acidic compounds are known to accelerate the rate of sediment formations in diesel fuels [11]. Thiols (relatively weak acids) under oxidation can form sulphonic acids which have been shown to catalyze the addition reaction of phenalenone to alkyl indoles to form a precipitate [12-13].

Other physical and chemical analyses of the low coal and high coal naphtha fractions indicated that naphtha from the low coal run had slightly lower density, viscosity and aromaticity compared with the high coal naphtha. Nitrogen and oxygen contents of the low coal naphtha were substantially lower than the high coal naphtha indicating that the main source of nitrogen and oxygen in the latter is from coal. However, the sulphur content in the high coal naphtha is lower due to the lower sulphur content of the coal compared with the oil feedstock. The aniline point of the high coal naphtha was also slightly lower which may reflect on the slightly higher aromaticity of this fraction compared with the low coal naphtha. The boiling point distributions of the naphtha fractions determined by simulated distillation were not significantly affected by the coal concentration in the original feedstock.

The light gas oil fraction from the 5 wt % maf coal run had relatively lower density, viscosity, aromaticity and a higher aniline point compared with the light gas oil fraction from the 30 wt % maf coal run. The light gas oil fraction from the high coal run, similarly to the naphtha fraction, had higher nitrogen and oxygen contents but less sulphur compared with the low coal run light gas oil fraction. Also, similarly to the naphtha fraction, the boiling point distribution of light gas oil fractions did not change significantly from the low to the high coal run.

A comparison of the initial properties of the heavy gas oil fractions from low and high coal runs showed that the heavy gas oil obtained in the low coal run had lower density, viscosity, nitrogen, oxygen but higher sulphur compared with the high coal run. The aromaticity and the metal contents of both distillates were similar and the boiling point distributions of the heavy gas oils were not significantly affected by increasing the coal concentration in the feed.

From the above discussion it is clear that increasing the coal concentration in the coprocessing feedstocks resulted in an increase in concentration of coal-derived liquids in the distillate fractions. This higher proportion of coal-derived liquids may have negative effects. These effects will be discussed in the stability of primary coprocessing distillates.

STORAGE STABILITY

The results of accelerated storage stability tests on low and high coal naphtha and light gas oil fractions are shown in Tables 3 to 7. These tests were carried out in 4-week intervals up to 16 weeks. Each sample was tested in duplicate. The filterable sediment results are shown in Table 3. For the naphtha fractions very little or no filterable sediment was formed during the 16 weeks. The sediment formation increased in the light gas oil fractions and more sediment was formed in the high coal light gas oil fraction. For the heavy gas oil fractions no difference occured in the amount of sediment formation after 16 weeks.

The formation of adherent gum or adherent sediment shown in Table 4 was more noticeable and again the high coal naphtha produced more (almost double) adherent gum than the low coal naphtha and the amount increased with time. However, the low coal light gas oil produced substantially more adherent gum compared with the high coal light gas oil fraction and the amounts in both cases increased during the test. For heavy gas oil fractions significantly higher amounts of adherent gum was formed from the high coal sample after 16 weeks compared with the low coal heavy gas oil fraction (Table 4). Different mechanisms were involved in sediment formation in the different boiling fractions. It has been suggested [4] that in light fractions, sediments are formed via oxidation reactions and in heavier fractions, sediments are formed mainly through polymerization reactions. The naphtha fraction from the high coal run contains a relatively higher concentration of coal-derived liquids which may include chemicals such as indans and tetralins. These compounds are known to play an important role in fuel degradation [14]. For light gas oil fractions it is speculated that because of the higher sulphur content in the low coal light gas oil, these compounds are oxidized to form higher concentrations (relative to the high coal gas oil fraction) of acids that accelerate the condensation (polymerization) reactions leading to sediment formation.

Existing gum (soluble gum) formation is shown in Table 5. Each sample bottle was analyzed at least twice. Good repeatability was obtained in each case. The numbers reported in this table are the average of two determinations. All fractions contained relatively high amounts of existing gum and the amount increased as the boiling point of the fractions and coal concentration of the feedstock increased. The amount of existing gum did not change significantly for low coal naphtha as a function of time and for high coal naphtha some increase was observed up to week 12 then it dropped at week 16. There was a substantial increase in the existing gum content in the low coal light gas oil up to week 12 and a slight drop occured at week 16. For the high coal light gas oil a large increase in existing gum content was observed during the 16 week test. Since the data for week 16 appeared to be questionable at least for the low and the high coal naphtha and the low coal light gas oil, the existing gum test (D381) was repeated for these samples (the repeat tests were carried out three weeks after the original measurement). The new data are shown in parentheses in Table 5. Although the values for the low coal naphtha and light gas oil fractions did not change significantly, higher numbers were found for the high coal distillates.

The results of solvent (heptane) washed gums obtained for the low and high coal naphtha are shown in Table 6. Initially the high coal naphtha had almost twice the solvent washed gum compared with the low coal naphtha. Although the amount of washed gum did not change significantly during 12 week test for the low coal naphtha, some increase was observed for the high coal naphtha. At the present we consider the results for week 16 questionable.

Figure 1 plots total gum (sediment, adherent and existing) versus weeks of storage at 43°C for the naphtha and light gas oil fractions. For the heavy gas oil fractions, total sediment plus adherent gum is plotted in Fig. 1 for week 16 only. In all cases distillates from the higher coal runs produced more gum. More total gum was formed in the heavier fractions. A similar trend has been observed for tar sands gas oil up to week 16 but the rate of total gum formation accelerated after sixteen weeks [5].

The effect of 43°C storage stability test on total acid number is shown in Table 7. Little or no changes were observed in total acid number during the 16-weeks storage. The higher total acid content in the distillates obtained in the higher coal concentration run is, at least in part, responsible for higher gum formations in these fractions. It has been shown that the concentration of phenolic (acidic) compounds in coprocessing naphtha increased as the coal concentration in the initial feedstock was increased [15]. Phenolic compounds are known to contribute to sediment formation in diesel fuels [16].

The most significant changes in the chemical and physical properties of the distillate fractions occurred in the heavy gas oil fractions during the 16-week storage. A significant increase in viscosities of both low and the high coal heavy gas oils was observed. The increase for the high coal heavy gas oil was more pronounced. Also, a large increase in aromaticity of the high coal and a modest increase in aromaticity of the low coal heavy gas oil fractions were observed.

CONCLUSIONS

The storage stability of primary coprocessing distillates (naphtha, light gas oil, heavy gas oil) was studied as a function of coal concentration. From their initial physical and chemical properties, it was predicted that the distillates obtained in coprocessing using a higher concentration of coal in the feedstocks would be less stable. A substantial amount of sediment and gum was formed during the 16-week storage of all distillates tested at 43°C. The amount of solids and soluble gum was increased as a function of time, boiling point of fractions and the coal concentration of the feedstocks. The relative instability of distillates obtained from feedstocks containing higher coal concentration was, at least in part, related to the higher content of acidic compounds in these distillates compared with distillates obtained from feedstocks containing less coal. Only the naphtha fraction from the high coal run had a better copper corrosion rating due to the lower sulphur content of this fraction compared with the naphtha fraction from the low coal run.

Most physical and chemical properties of the naphtha and light gas oil fractions did not change at the experimental conditions used. A significant increase in terms of viscosity and aromaticity occurred in the heaviest fractions (heavy gas oils).

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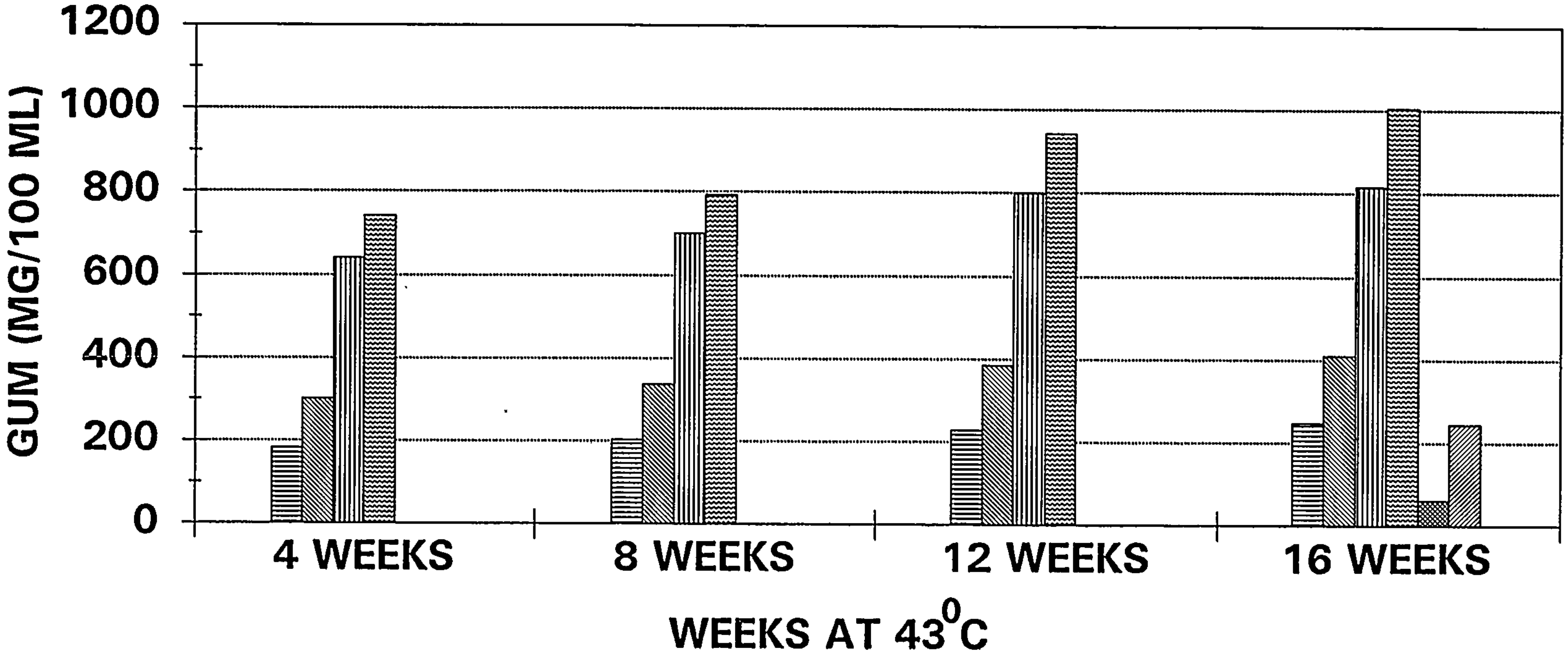

Fig. 1 - Effect of coal concentration on storage stability of coprocessing distillates

Table 1 - Comparison of properties of coprocessing distillate fractions with commercial synthetic crude*

Analysis (wt %)	Naphtha			LGO			HGO		
	CPL[1]	CPH[2]	SCO[3]	CPL[4]	CPH[5]	SCO[6]	CPL[7]	CPH[8]	SCO[9]
Sulphur	0.58	0.47	0.00022	2.12	1.64	0.04	2.03	1.63	0.24
Nitrogen	0.75	0.17	0.00011	0.25	0.47	------	0.50	0.77	0.155
Oxygen	<0.5	1.10	------	<0.5	1.80	------	<0.5	0.55	------

* ref. 4.

[1] Coprocessing naphtha low coal (IBP-185°C)
[2] Corpcessing naphtha high coal (IBP-185°C)
[3] Synthetic crude oil naphtha (82-177°C)
[4] Coprocessing LGO low coal (185-335°C)
[5] Corpcessing LGO high coal (185-335°C)
[6] Synthetic crude oil mid-distillate (177-343°C)
[7] Coprocessing HGO low coal (335-525°C)
[8] Corpcessing HGO high coal (335-525°C)
[9] Synthetic crude oil gas oil (343°C+)

Table 2 - Properties of distillate fractions

Test	ASTM method	Low Coal			High Coal		
		Naphtha (IBP-185^{0}C)	LGO (185-335^{0}C)	HGO (335-525^{0}C)	Naphtha (IBP-185^{0}C)	LGO (185-335^{0}C)	HGO (335-525^{0}C)
Oxidation stability (min)	D525	>2700	>2700	>2700	>2700	>2700	>2700
Copper corrosion (3 h at 100^{0}C)	D130	3b	la	1a	3a	1a	1a
Accelerated stability (16 h at 95^{0}C) (mg/100 mL)	D2274	ND*	76	ND	ND	83	ND
Total acid number (mg K0H/g)	D974	0.05	0.14	0.16	0.20	0.51	0.33

*ND = not determined

Table 3 - 43°C storage stability test - filterable sediment (mg/100 mL)

Distillate	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	0.24 ± 0.14	-0.52	-0.43 ± 0.51	0.05 ± 0.21
High coal naphtha	0.02 ± 0.075	-0.95 ± 0.90	-1.02 ± 0.19	-0.12 ± 0.77
Low coal LGO	-0.22 ± 0.07	0.68 ± 0.63	1.06 ± 0.35	1.24 ± 0.22
High coal LGO	1.09 ± 0.54	3.50 ± 0.58	2.90 ± 0.59	3.10 ± 0.27
Low coal HGO	--------	--------	--------	53.55 ± 0.35
High coal HGO	--------	--------	--------	52.25 ± 0.85

Table 4 - 43°C storage stability test - adherent gum (mg/100 mL)

Distillate	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	36.6 ± 2.9	69.5	92.9 ± 1.2	120.5 ± 1.5
High coal naphtha	67.3 ± 1.8	105.3 ± 5.2	138.5 ± 5.1	209.3 ± 7.9
Low coal LGO	12.7 ± 0.4	39.8 ± 0.9	56.8 ± 1.1	83.7 ± 1.6
High coal LGO	0.72 ± 0.28	1.74 ± 0.22	1.40 ± 0.8	6.7 ± 0.5
Low coal HGO	--------	--------	--------	7.50 ± 0.35
High coal HGO	--------	--------	--------	191.4 ± 18.6

Table 5 - 43°C storage stability test - existing gum, ASTM D381 (mg/100 mL)

Distillate	Initial	4 weeks	8 weeks	12 weeks	16 weeks (repeat)
Low coal naphtha	132.8 ± 3.8	145.0 ± 15	132.6	135.3 ± 2.7	126.8 ± 0.2 (120)
High coal naphtha	212.5 ± 3.3	232.5 ± 2.3	232.2 ± 5	246.1 ± 0.9	200.5 ± 1.5 (250)
Low coal LGO	554.0 ± 28.8	627.0 ± 5.4	660.1 ± 23.7	742.1 ± 19.9	730.5 ± 0.7 (716)
High coal LGO	642.0 ± 30.8	738.7 ± 22.1	787.0 ± 16.4	938.0 ± 9.1	994.3 ± 1.1 (1070)

[*] Repeat of D381 test (average of two determinations)

Table 6 - 43°C storage stability test - solvent washed gum*, ASTM D381
(mg/100 mL)

Distillate	Initial	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	80.0	95.4 ± 10.4	86.8	91.2 ± 0.8	89.1 ± 0.5
High coal naphtha	179.4	196.9 ± 0.1	208.1 ± 4.3	213.1 ± 1.2	173.2 ± 1.8

*Heptane

Table 7 - Effect of 43°C storage stability test on total acid numbers
(ASTM D974)

Distillate	Initial	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	0.05	0.025 ± 0.005	0.06	0.025 ± 0.005	0.035 ± 0.005
High coal naphtha	0.20	0.18 ± 0.0100	0.18 ± 0.005	0.19 ± 0.020	0.16 ± 0.010
Low coal LGO	0.14	0.15 ± 0.005	0.15 ± 0.015	0.14 ± 0.000	0.19 ± 0.015
High coal LGO	0.51	0.47 ± 0.010	0.53 ± 0.005	0.57 ± 0.025	0.56 ± 0.005