IASH '97, the 6th International Conference on Stability and Handling of Liquid Fuels

Vancouver, B. C., Canada
October 12-17, 1997

ABILITY OF FUEL AND WATER SOLUBLE BIOCIDES TO PREVENT MICROBIAL SUCCESSION CHANGES TO OXYGENATED GASOLINE AND SYNTHETIC TANK WATER BOTTOM CHEMISTRY IN LABORATORY MICROCOSMS

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Abstract

Biodeterioration has a cost impact that is only beginning to be recognized and quantified. The ability of two biocides to prevent microbial succession changes to oxygenated gasoline was followed for seven-months in replicated microcosms. Three concentrations of each biocide were evaluated representing the maximum allowable dose, the manufacturer's recommended dose, and the lowest effect dose. Fuel and water phase samples were taken at day 0, 0.25, 1, 3 and 7 months and analyzed for gasoline hydrocarbons and pH, TDS, alkalinity, dissolved oxygen, nitrite and nitrate nitrogen, respectively. Gasoline and aqueous phases were characterized with respect to total heterotrophs, total aerobes, total anaerobes, acid producing and sulfate reducing bacteria, and catalase activity. Both biocides initially provided protection against changes in gasoline quality and minimization of rag layer development. However, by one month, we observed significant performance differences between the two products. Sulfate reducing bacteria were the most difficult to control of the microbial groups investigated. Threshold concentrations of microorganisms that correlate with negative fuel impacts will be discussed as well as the impacts of biocides on corrosion rate and fuel filterability.

6th International Conference on Stability and
Handling of Liquid Fuels
Vancouver, B. C., Canada, October 13-17, 1997

A NEW ON-SITE QUANTITATIVE TEST FOR MICROORGANISMS IN FUEL

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Abstract

Traditional viable count technology for determining microbial numbers in aqueous samples, involves incubation and assesses microbial numbers as colony forming units (cfu), i.e. visible nodules of microbial growth. Methods fall into two categories, 'shake' plates in which samples are dispersed in nutritive molten agar which is solidified by cooling and then incubated or by spreading samples onto solid nutritive agar plates. Neither method is suitable for non-aqueous samples. Microbes are recovered from these by membrane filtration and the membrane is then placed on top of a nutritive agar plate. Alternatively the sample is emulsified in water before a conventional viable count procedure. The increasing demand for reliable viable counts on fuel samples has lead to a membrane filtration procedure, IP385/95, and to an emulsification procedure AFNOR MO7070/92. The former is unsuitable for on site use and although the latter can be coupled to a Dip-slide test it inherits the errors of this procedure and lacks sensitivity. The methodology described in this paper was a direct response to the need for a sensitive, quantitative on-site microbiological test for fuel but the technology can be applied to any aqueous and non-aqueous sample. It allows the "shake" plate concept to be used in the laboratory or on-site.

In principle a nutritive solution is gelled with thixotropic and/or pseudo-plastic agents instead of agar. An aqueous or non-aqueous sample can be dispersed in the gel by shaking and the gel is allowed to re-set as a flat horizontal layer. During incubation microbes develop into visible colonies comparable to colony formation in 'shake' plates. In the preferred configuration for fuel testing c.16ml of gel is dispensed into screw capped rectangular glass containers c. 65ml capacity. The size of the sample is selected according to the sensitivity required but the volume of gel must be kept in proportion; 0.25ml of fuel is normally tested. During incubation a sensitive redox indicator is reduced to a coloured formazan within the microbial colonies and assists enumeration. The accuracy is similar to a shake plate. Very large numbers of microbes produce coloured formazan within a few hours - a real time test. The gel composition described has been formulated so that fuel samples emulsify and completely disperse but it is also suitable for aqueous samples. The formulation has been used to test diesel fuel and aviation kerosene; the results are comparable to the methods IP385/95 and AFNOR MO7070/92.

1. Introduction

The incidence and consequences of microbial spoilage of distillate fuels is well documented and has been featured in all "Stability and Handling of Liquid Fuels" conferences. There have been inherent problems of standardising procedures for sampling, sample handling and testing fuels and interpreting results but most issues have now been addressed in "Guidelines for the Investigation of the Microbial Content of Fuel Boiling Below 390°C and Associated Water" published by the Institute of Petroleum, London in 1996 (1). A quantitative laboratory test based on a membrane filtration procedure, IP385/95, is widely accepted as a reference method (2). It up-dates and extends the previous method IP385/88. The French procedure AFNOR MO7070-1992 (3) is more suitable for on-site use a it utilises a Dip-slide to test emulsified fuel but it lacks sensitivity and is semi-quantitative. On-site tests have been reviewed recently by the International Bunker Industry Association (4) but most tests have been complex, semi-quantitative and have lacked sensitivity. Whilst they should all identify a problem fuel as suffering from microbial contamination the real value of an on-site test is to give quantitative early warning so that avoidance or remedial measures can be instituted in good time and their efficacy monitored.

The methodology described in this paper was a direct response to the need for a sensitive, quantitative on-site microbiological test for fuel but the technology can be applied to any aqueous or non-aqueous sample.

Inspired by a particularly glutinous bottle of tomato sauce an attempt was made to substitute a thixotropic gelling agent for agar in a typical tryptone soya agar microbiological culture medium. It was hoped that a sample could be dispersed in the gel by vigorous shaking and that the gel would then re-set for conventional incubation and colony counting. A tetrazolium redox indicator was included; these indicators change from colourless salts to brightly coloured formazans in the presence of microbial colonies and hence aid colony enumeration. Initially the gelling agent was Xanthan; aqueous suspensions of bacteria were diluted in a logarithmic series and each level of dilution used to inoculate a gel tube. The results were very encouraging, not only indicating that the technology could be developed to equate to conventional plate counts but also that large numbers of organisms would reduce the tetrozolium indicator in real time.

A development programme was planned and initiated to address the following issues:

Characterisation and selection of gelling agent(s)
Optimisation of nutrient formulation
Design of the redox indicator system
Configuration of the test
Validation against conventional quantitative methods
Field evaluation.

The work was supported by EU and Welsh Office grants. It was anticipated that the work would be primarily directed to developing a test for water associated with fuel; by implication fuel in contact with infected water would also be infected. It was soon apparent that there were good possibilities for extending the project for the direct enumeration of microbes in the fuel phase and this exciting prospect was vigorously pursued. The intellectual property has been protected by patent applications and the product is referred to as SMARTGEL.

2. Characterisation and selection of gelling agent(s)

The desirable characteristics were:

Clear and colourless .
Sets in a firm gel at incubator temperatures with discrete colonies after incubation.
Minimal water expression (hysteresis) when set.
Not rapidly biodegraded during incubation.
Amenable to heat sterilisation.
Readily liquefied by shaking but then takes 5-30 seconds to re-set.
Water phase samples disperse readily; oil phase samples emulsify.

The following agents have either thixotropic (progressively become more viscous after mechanical stress) or pseudo-plastic (deform only at the time of stress) properties. The list is not exhaustive.

Xanthan; tragacanth, guar, gum arabic, alginates, ghatii, cellulose derivatives, carrageenan, starch, dextrin, pectin, carob, chitin, gelatin.

Most were tested alone and in combination. The preferred combination is xanthan, carrageenan and agar and it meets all of the criteria listed.

3. Optimisation of nutrient formulation

The nutrient components were selected along conventional lines to support the growth of Gram negative bacteria, yeast's and moulds, all of which can cause operational problems when contaminated fuel is used. A pH of c. 6.1 was selected, not only as a compromise pH suitable for most microorganisms but also to stabilise the redox indicator system. Pyruvic acid was used to enhance formazan production and it also stimulated mould growth. For test users who might require a gel which suppressed bacteria selectively but allowed yeast/mould growth, oxytetracycline was incorporated in one version of the gel (SMARTGEL M) and the pH was lowered to 5.5. The preferred nutrient formulation contains tryptone, peptone, glucose and pyruvic acid.

4. Design of the redox system

The following redox indicators were considered but not all were tested. Some were tested in combinations; some were evaluated with coupling agents such as menadione which enhance the speed of re-action.

INTV	Iodonitrotetrazolium violet	Oxygen Insensitive
INTB	Tetranitrotetrazolium blue	|
NTB	Nitrotetrazolium violet	|
NT	Neotetrazolium chloride	|
TBC	Tetrazolium blue chloride	|
TV	Tetrazolium violet	↓
TTC	Triphenyl tetrazolium chloride	Oxygen Sensitive

All are colourless and are reduced by microorganisms to form coloured formazans within the colonies, thus making them quickly and easily visible. The oxygen sensitive indicators are most re-active both with microorganisms and chemical reducing agents.

The final selection was iodo-nitro-tetrazolium violet which reduces to a purple formazan. Some fuels contain anti-oxidants and a pale colouration develops as soon as such a fuel is added to the gel. This does not in fact mask the deeply coloured colonies but it was felt advisable to have a reserve choice, tetrazolium violet which was not affected by anti-oxidants but colony colouration was less intense particularly for yeasts and moulds.

5. Configuration of the test

Various configurations of container, gel volume and air space were investigated. Complete compatibility of the container with fuel restricted the choice of container. The preferred fuel sample size of 0.25ml (to give a lower detection limit of 4 microbes ml^{-1}) influenced the gel volume selected as the gel opacity increases when the fuel is incorporated in it.

An appropriate configuration has been achieved by using 16ml of gel in 60ml volume glass screw capped flat rectangular bottles. The gel is allowed to set as an even, large flat film. The sequence of testing is illustrated in Fig 1.

6. Validation against conventional quantitative methods

Validation has been primarily directed towards fuel tests; field samples which had been submitted for routine laboratory tests by IP385/95 were tested and also fuel tank simulations. IP385/95 Part A is a membrane filtration test in which between 1ml and 100ml fuel is filtered. The membrane is transferred to a nutrient agar plate and this is incubated. Colonies develop on the membrane surface. If the fuel is heavily contaminated it is not possible to count colony forming units (cfu); there is a Part B to the test in which the organisms on the membrane are re-suspended by vortexing in 1/4 strength Ringers solution and conventional total viable counts (TVC) are carried out on this. If both Part A and B are carried out on the same sample and both yield usable counts of cfu it is generally found that the Part B procedure delivers the highest TVC - presumably because of the mechanical agitation involved. In the test AFNOR M07070/92 2ml fuel is emulsified with 18ml aqueous Tween 80; the emulsion is then Dip-slide tested or a conventional TVC carried out. The result is often an order of magnitude greater than either part of IP385/95, presumably because of the well known ability of Tween 80 to separate and disperse microbial aggregates, particularly fungal spores. There is thus no "right" answer for a quantitative microbiological test on fuel; the result must be interpreted in relation to the test method.

In Table 1A results are given when three guel samples (submitted to ECHA for routine testing) were tested by IP385/95 Part B and the thixotropic gel procedure.

In Table 1B results are given when fuel emulsions of contaminated fuels were made as per AFNOR M07070/92 and dilutions of the emulsion tested by conventional spread plates and by the SMARTGEL method.

Referring to Table 1A the SMARTGEL technique yields a result usually marginally lower than Part B of IP385/95; this was anticipated.

Referring to Table 1B the SMARTGEL technique yields results broadly similar to spread place TVC's on AFNOR emulsions.

The same gel formulation was used for tests on aqueous fuel tank samples. In Table 2, four fuel tank water bottoms from laboratory simulations were serially diluted in phosphate buffered saline and each dilution was tested by spread plates and SMARTGEL.

The results are typical of the many comparative tests carried out. These comparisons have included commercial oil in water emulsions, lubricating and hydraulic oil.

7. Field Evaluation of Fuel Quality

Batches of SMARTGEL were released for field evaluation by major petroleum companies and fuel users. The results were favourable but the instructions have been modified to indicate that after conducting the test the SMARTGEL bottles must not be substantially disturbed during incubation. SMARTGEL tests are now being marketed in Europe and ECHA has withdrawn its previous semi-quantitative test, the Sig Fuel test.

To complete the SMARTGEL test kit, sterile disposable syringes (1ml x 0.01) are supplied. The recommended test sample volume for visually clean fuel is 0.25ml which gives a quantitative detection range of 4-1000 microbes per ml (4×10^3 - 1×10^6 per litre); above this range the result is semi-quantitative (see Interpretation chart, Fig 2). The test can be used to test lubs and hydraulics; the recommended test sample volume is 0.01 ml and this can be measured with one of the sterile disposable 10 $\mu\ell$ loops supplied with the kit. The quantitative detection range is 10^2 - 3×10^4 microbes per ml.

A tank bottom water test is always informative and a 10 $\mu\ell$ loop can be used to measure and test a sample of this.

The sample volumes are recommended so that the test result falls into a range which can be readily interpreted. If fuel is known to be heavily contaminated the sample volume tested can be reduced. Bulk fuel ex-refinery should be of a very good microbiological quality and in normal practice a number of layer or running samples could be available for testing. Individual SMARTGEL test results might be negative but results could be pooled to yield a notional 'average' result. For example if eight 0.25 ml samples were tested with colony count results of

1,0,0,2,1,0,0,1

the notional average count would be 1,000 per litre.

Very large numbers of microbes reduce the redox indicator in SMARTGEL to a pale purple colouration throughout the gel in about two hours thus providing a real time test for very heavy contamination. A slight chemical reduction can take place by fuel anti-oxidants but this does not mask the detection of the intensely coloured colonies of microbes.

A number of semi-quantitative on-site tests have been available for some years and the detection range of these (as quoted in the suppliers literature) is given in Table 3. In some cases they would be of little use as early warning tests as the lower detection limit is too high.

8. Standards

The Institute of Petroleum Guidelines (1) do not propose rigid standards but emphasise that limit values should be related not only to the sampling location but also to the intended use of the fuel and any risk factors - for example long term storage.

In fact because of the previous lack of a quantitative on-site test, little is known of norms for the variety of situations which exist in distribution and use. Problem fuels have been investigated by many laboratories but the effort and cost of submitting non-problem fuels for laboratory testing has been difficult to justify. The availability of a simple quantitative on-site test should stimulate interest in establishing norms and for setting Warning and Action limits appropriate to individual situations.

9. Acknowledgements

After initial development work the R&D has been supported by Welsh Office/EU funds in the form of a competitive SMART award - hence the designation SMARTGEL. Further support has been given in the form of a SPUR award.

This support is gratefully acknowledged.

We also appreciate the interest and comments of the companies who have carried out field evaluation.

10. References

1. Guidelines for the Investigation of the Microbial Content of Fuel Boiling Below 390°C and Associated Water, Institute of Petroleum, London, 1996.

2. Determination of the Viable Microbial Content of Fuels and Fuel Components Boiling Below 390°C - Filtration and Culture Method. IP385/95. Institute of Petroleum, London, 1995.

3. AFNOR M07070: 1992. Combustibles pour moteurs Diesel et pour installations de chauffage domestique - Recherche des microorganismes par tests sur gélose, Association Française de Normalisation, 1992.

4. On Board Test Kits. International Bunker Industry Association Ltd., anon, 1996.

Table 1

COMPARISON OF VIABLE COUNT TESTS ON ROUTINE FUEL SAMPLES RECORDED AS COLONY FORMING UNITS (CFU) USING SMARTGEL AND STANDARD METHODS

METHODS

1A Comparison of IP 385/95B and SMARTGEL

FUEL SAMPLE	IP385B Total cfu l^{-1}	SMARTGEL Total cfu l^{-1}
1	1.52×10^6	1.31×10^6
2	2.44×10^6	9.7×10^5
		3.12×10^6 (replicate)
3	3.65×10^6	9.1×10^5

1B Comparison of AFNOR M07070/92 and SMARTGEL evaluations of the AFNOR emulsions

Fuel emulsions (2ml of fuel emulsified in 18ml of 0.1% Tween 80) were tested by spreading 0.1ml aliquots onto Tryptone Soya agar and Malt Extract agar and by dispersing 0.1ml aliquots into SMARTGEL and SMARTGEL M. Serial tenfold dilutions were similarly tested. Differentiation into bacteria (B) moulds (M) and yeasts (Y) was visual only but was aided by the selective nature of the media used.

	SPREAD PLATES cfu l^{-1}		SMARTGEL cfu l^{-1}	
AFNOR Emulsion - FUEL 4	1.17×10^{10}	B	7.9×10^9	B
AFNOR Emulsion - FUEL 5	3.7×10^9	B	2.3×10^9	B
	3.3×10^7	M	1.5×10^7	M
	2.21×10^8	Y	2.26×10^8	Y

Table 2

COMPARISON OF VIABLE COUNT TESTS ON WATER BOTTOMS IN SIMULATED FUEL TANKS RECORDED AS COLONY FORMING UNITS (CFU) USING SPREAD PLATES (TRYPTONE SOYA AGAR) AND SMARTGEL

SAMPLE	SPREAD PLATES cfu ml^{-1}	SMARTGEL cfu ml^{-1}
Fuel 1 Water Bottom	7.88×10^6	7.30×10^6
Fuel 1 Replicate	8.05×10^6	-
Fuel 2 Water Bottom	1.40×10^6	2.27×10^6
Fuel 2 Replicate	1.73×10^6	-
Fuel 3 Water Bottom	2.95×10^7	6.6×10^7
Fuel 4 Water Bottom	1.94×10^8	3.37×10^8
Fuel 4 Replicate	2.86×10^8	2.2×10^8

Table 3

COMPARISON OF COMMERCIAL ON-SITE MICROBIOLOGICAL TESTS FOR FUEL

Test/Method	Detection Range/Accuracy Microbes (cfu) per litre
AFNOR M07070/92. Emulsify 2 ml of fuel with 18 ml water. Test with Dip-slide.	10^6 - 10^9 Semi-quantitative
Bugbuster. Extract fuel with water and inject 1ml aliquots into nutrient bottles.	10^3 or more Go/NoGo
Liquicult (Humbug). Inject 5 ml of fuel into nutrient bottles.	10^5 - 10^9 bacteria 10^4 - 10^8 yeasts/moulds Semi-quantitative
SMARTGEL. Shake 0.25 ml of fuel directly into bottle of gel*.	4×10^3 - 1×10^6 quantitative $> 10^6$ semi-quantitative

* Range can be altered by using other measured sample volumes.

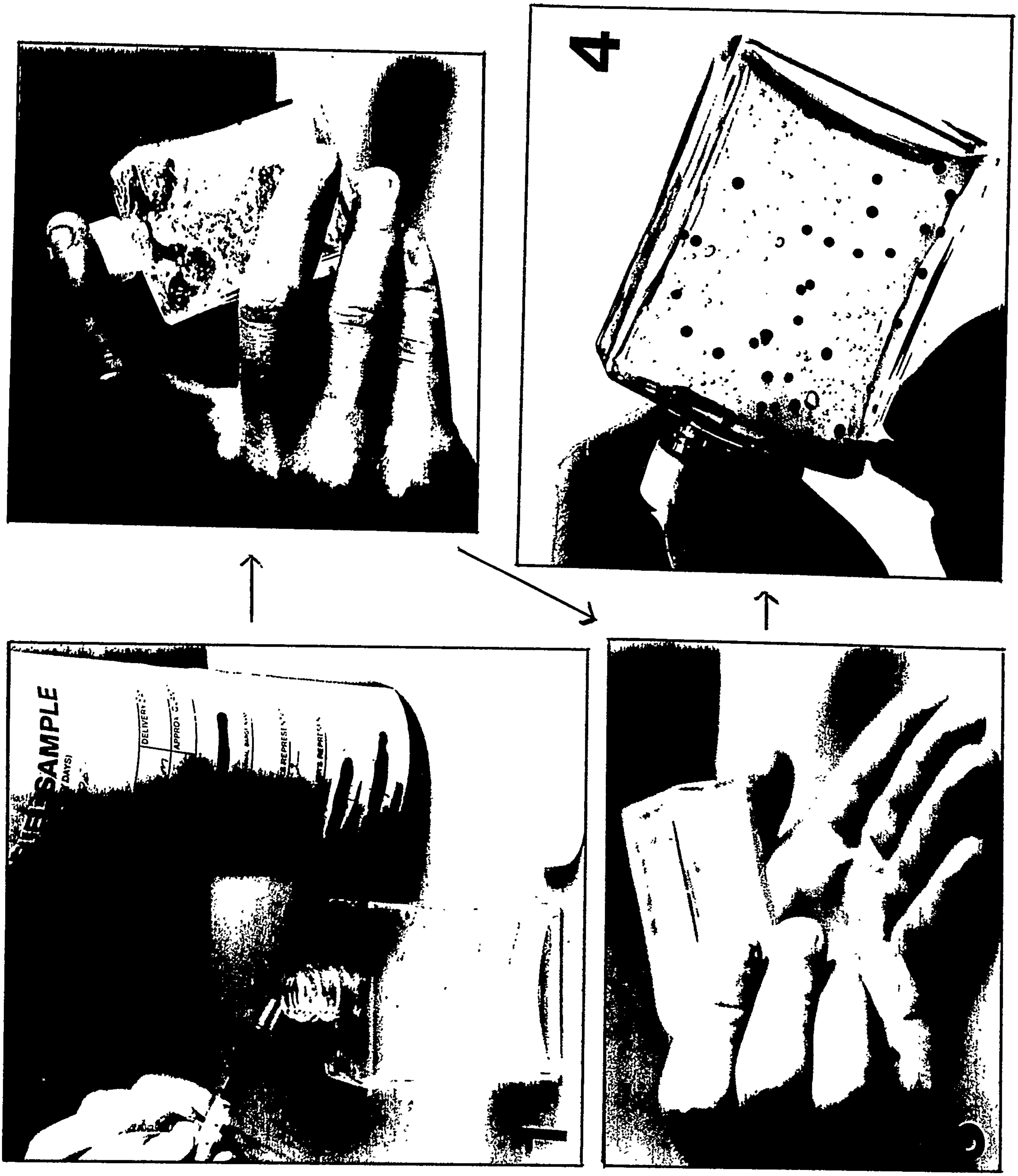
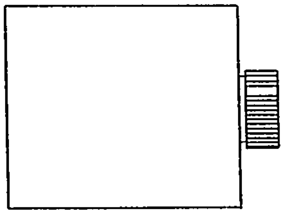
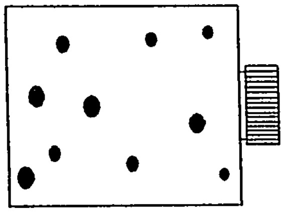
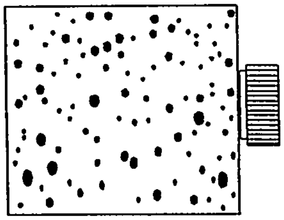
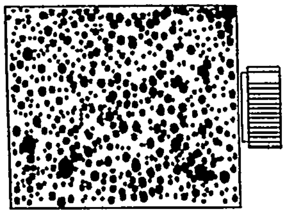
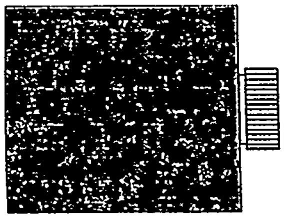


Fig. 1. Sequence of actions for the use of SMARTGEL to test fuel.

1. Transfer 0.25 mL of fuel to SMARTGEL with a sterile, disposable syringe. Re-cap gel bottle. **2.** Tap sharply to "crack" gel structure then shake vigorously for ca. 30 s. Shake liquefied gel into bottom of bottle. **3.** Hold bottle flat and tap on palm of hand until an even layer of gel forms. Incubate at 28-30°C for up to 4 days with the gel layer on the bottom of the bottle. **4.** Count purple colonies against a white background, marking them with a felt tip pen as you count. Calculate or estimate the number of cfu l^{-1} of fuel using the interpretation chart if necessary.

Fig 2. Interpretation chart for on-site use of SMARTGEL for estimating numbers of CFU in fuel and tank water bottoms.

GEL RESULTS CHART

	Volume Tested	Nº of cfu	Sample Contamination
	0.25 ml of fuel $10\mu l$ of water	0 0	Less than 4000 cfu per litre Less than 100 cfu per ml
	0.25 ml of fuel $10\mu l$ of water	10 counted 10 counted	4 × 10^4 cfu per litre 1000 cfu per ml
	0.25 ml of fuel $10\mu l$ of water	100 counted 100 counted	4 × 10^5 cfu per litre 10,000 cfu per ml
	0.25 ml of fuel $10\mu l$ of water	1000 estimated 1000 estimated	4 × 10^6 cfu per litre 100,000 cfu per ml
	0.25 ml of fuel $10\mu l$ of water	Estimated by chart comparison Estimated by chart comparison	4 × 10^7 cfu per litre or above 10^6 cfu per ml or above *

Note: numbers of microorganisms are normally expressed per litre of fuel and per ml of water.

* Very large numbers of microorganisms in the water sample (10^7cfu/ml & above) may induce a colour change in only a few hours.

If different volumes of fuel or water are tested the calibrations and estimation of cfu are adjusted accordingly.

6th International Conference
on Stability and Handling of Liquid Fuels
Vancouver, B.C., Canada
October 13 - 17, 1997

STABILITY AND HANDLING OF SASOL SEMI-SYNTHETIC JET FUEL

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Abstract

Jet fuel made from shale and coal by various methods employing hydrogen treatment and polymerization (as used in the Sasol Fischer-Tropsch gas/syncrude process) usually results in hydrocarbon fuel with very high thermal stability and negligible levels of sulphur and aromatics. Early work during the 1980's on both shale- and coal- derived jet fuel identified two drawbacks to the potential commercial use of these fuels. These were the fuel's poor lubricity properties and the shrinkage of seals previously wetted by crude oil-derived fuels. Additional concerns expressed at the time were the fuel's additive response and its capacitance, or dielectric constant, when used in density correlations. In order to produce a more acceptable fuel for use in commercial aircraft operating out of Johannesburg International Airport, Sasol will blend a synthetic jet fuel component with crude oil-derived jet fuel to increase the blend's aromatic content. This will improve both the elastomer compatibility and the lubricity of the fuel. These and other properties of the synthetic jet fuel component and the semi-synthetic jet fuel blend are discussed in this paper. Other properties studied included the fuel's gum and peroxide formation tendencies which were evaluated for both the neat and additised fuel using accelerated stability tests to confirm antioxidant additive response in the fuel. The compatibility of elastomeric materials used in fuel handling equipment, such as the hoses on ground equipment and pump seals in aircraft components, with the semi-synthetic jet fuel was also confirmed. Finally biocide additive efficacy in the synthetic fuels was determined. It was found that the Sasol synthetic jet fuel is an excellent blending component to blend Sasol semi-synthetic Jet A-1.

INTRODUCTION

The production of synthetic fuels is not new to Sasol. Sasol started to produce synthetic fuel from coal in 1955 at their synthetic fuel plant in Sasolburg, South Africa. The decision to produce fuels from coal at that time was for strategic reasons as South Africa has no natural crude oil reserves. The process used by Sasol to produce synthetic fuels can briefly be described as follows:

- Low-grade coal is gasified to produce tar liquids and synthesis gas (CO and H_2).

- Synthesis gas is converted into liquid hydrocarbons via the Fischer-Tropsch process.
- Synthetic crude oil, with a carbon distribution in the range from C_1 to C_{40}, is then refined producing the full slate of products usually produced by a crude oil refinery.

The products produced have very low sulphur levels as sulphur is a poison for the catalyst used in the Fischer-Tropsch process and is therefore removed after the gasification step.

The production of synthetic fuels in South Africa was scaled up during the energy crisis in 1979 when two new plants, Sasol 2 and Sasol 3, were built. By 1997 synthetic fuel represented 30 % of the total volume of liquid fuels produced in South Africa. The use of synthetic fuels in all applications, except for aviation fuel, is not new and field experience with these fuels for the last 18 years has shown that the product performs excellently with major benefits for both the user and the environment.

Air traffic to South Africa has increased significantly since 1994 and it is projected to continue to increase in the foreseeable future. The increase in air traffic is straining the availability of jet fuel at Johannesburg International Airport (JIA). Sasol proposes to increase the supply of Jet A-1 from the Natref refinery by blending a synthetic hydrocarbon stream, from its Secunda synthetic fuel refinery that conforms to jet fuel specification requirements into Natref crude oil derived jet fuel. The stream has been used as a diesel fuel blending component for the last 18 years. The result will be a blend of a synthetic hydrocarbon stream with the crude oil-derived Jet A-1 produced at Natref to yield a semi-synthetic Jet A-1 fuel.

At the start of this project, it was envisaged that a semi-synthetic Jet A-1 blend as well as a fully synthetic Jet A-1 would be investigated in order to get them qualified as commercial aviation fuel. It was however soon realised that it was not going to be easy to achieve this and the scope of the project was changed to get only the semi-synthetic Jet A-1 qualified.

The Joint Checklist, a specification with guidelines for participants in jointly operated fuel delivery systems, controls the quality of Jet A-1 in South Africa. It contains the strictest specifications for jet fuel as set out in the IATA, ASTM D1655, and Defence Standard 91-91 specifications.

PRODUCTION OF SASOL SYNTHETIC JET FUEL

The Sasol synthetic jet fuel production process starts with synthesis gas, produced by gasification of coal, which is converted via the Fischer-Tropsch process to liquid hydrocarbons ranging in carbon number from C_1 to C_{40}. The C_3 and C_4 olefins, which are separated using cold separation, are used as feed to the process used to produce the synthetic jet fuel component. Figure 1 shows the production scheme used to produce the synthetic component in more detail. The first step is the gasification of the coal to hydrogen (H_2) and carbon monoxide (CO). It is important to note that all the liquid tars and other contaminants, such as metals and sulphur, are removed before the synthesis gas is passed over an iron-based catalyst used in the Fisher-Tropsch process to yield a wide boiling range synthetic crude oil. The heavier material is used to make gasoline and diesel fuel and other streams are used for the production of petrochemicals.

The synthetic kerosene is produced from the C_3 and C_4 olefins that have been separated from the synthetic crude by cold separation. The olefins are then polymerized followed by hydrotreating and distillation to produce iso-paraffinic kerosene of the correct boiling range for jet fuel. The processes used to produce the synthetic jet fuel component is a standard refining process used by Sasol for over 15 years to produce illuminating kerosene and a blending component for diesel fuel.

FUEL PROPERTIES AND CHARACTERISTICS

Synthetic jet fuel component

The synthetic component is almost entirely composed of iso-paraffins although a few percent of normal paraffins are also present. What is significant is that jet fuel produced from crude oil also consists mainly of iso-paraffins. Typical properties of the synthetic jet fuel component are given in Table 1.

TABLE 1 : PROPERTIES OF THE SASOL SYNTHETIC JET FUEL COMPONENT

Property	Typical synthetic jet fuel component values
Density @ 20 °C, kg/m^3	760 – 775
Aromatics, vol %	0
Sulphur, ppm	< 10
Flash point, °C	42 – 57
Freezing point, °C	< -60
Viscosity @ -20 °C, cSt	3.2 - 3.5
Specific energy, MJ/kg	43.2 - 44.0
Distillation, °C:	
- IBP	160 – 175
- 50 %	175 – 195
- FBP	230 – 240
Smoke point, mm	32 - >50
Hydrogen content, mass %	15.06
BOCLE [1] Lubricity, mm WSD[2]	0.85 - 1.04

Note: 1 BOCLE = Ball on cylinder lubricity evaluator
2 WSD = Wear Scar Diameter

These properties are very similar to values for typical jet fuels. Density, which is below the minimum of 0,775 kg/ℓ at 15 °C, is the only property that does not meet the Jet A-1 specification requirements. The lubricity rating is not a specification requirement but a wear scar diameter of 0.85 mm is considered to be the maximum acceptable value. The synthetic component has many desirable features as a jet fuel including high hydrogen content, very low sulphur content, very low freezing point and exceptional stability.

Blend of synthetic and crude oil-derived jet fuels

Sasol considered the production of synthetic jet fuel in the early 1980's. Four properties were identified at that time as concerns by the aviation industry:

- Low lubricity
- Low fuel density
- Low volumetric energy density, i.e. MJ/ℓ
- No aromatics

Although energy density is not a specification requirement, a low value could restrict the range of an aircraft if it were volume limited for a certain flight. The specific energy of the fuel is, however, above the minimum limit of 42.7 MJ/kg.

The lack of aromatics was considered a possible cause for concern because aromatics cause nitrile (Buna-N) elastomers to swell, a property often taken into account in designing seals and gaskets. Changing from a high-aromatic fuel to a low-aromatic fuel has been known to cause some seals to shrink leading to fuel leakage.

Because of these concerns and recommendations from the engine and airframe manufacturers, it was decided to blend the synthetic component with crude oil-derived jet fuel to address all the issues mentioned above. Furthermore, blends of synthetic hydrocarbons with crude oil-derived hydrocarbons are specifically allowed in the ASTM D1655 fuel specification for Jet A-1 fuel.

As a further step to address the concerns and issues and to improve the acceptability of the fuel, Sasol had decided to impose additional restrictions on the Semi-Synthetic Jet Fuel:

- A minimum of 8 volume % aromatics will limit the impact of using fuels of varying aromatic content.
- The BOCLE lubricity rating will be reported.
- The maximum amount of the synthetic component will be 50 volume percent.

In all the work discussed below, two semi-synthetic blends were used. Semi-synthetic 1 (SS1), containing approximately 15 % aromatics, is a blend of 50 % of the synthetic component and 50 % crude oil-derived jet fuel. Semi-synthetic 2 (SS2), containing approximately 8 % aromatics, is a blend of 25 % synthetic component and 75 % crude oil-derived jet fuel.

ISSUES AND CONCERNS

Elastomer compatibility

The synthetic blending component is mainly iso-paraffinic containing a few percent of normal paraffins. No contaminants or other organic species such as aromatics, acids, and alcohols that could cause problems with elastomers are present.

Only a few elastomeric materials are used in fabricating sealing items such as O-rings, gaskets, diaphragms and bladders used in aircraft fuel systems. These are:

- Nitrile/Buna-N
- Fluorocarbon/Viton
- Fluorosilicone
- Neoprene (in some older systems)

Compatibility tests were conducted on O-rings consisting of Buna-N, fluorocarbon, and fluorosilicone. Limited compatibility tests were also carried out on various used O-rings from the main-engine fuel pump of a Boeing 737 aircraft supplied by South African Airways. Finally tests were conducted on a used refuelling hose from Johannesburg International Airport.

The compatibility of new Buna-N, fluorocarbon, and fluorosilicone with the semi-synthetic jet fuel blends was evaluated by comparing the effect of the fuel on the following properties of the elastomers:

- Mass change and volume change (ASTM D471)
- Tensile strength and Young's modulus (ASTM D412)

The results of the measurements of mass and volume change for the different materials, are shown in Figures 2 and 4 while Figures 3 and 5 present the results related to the tensile strength and Young's modulus of the elastomers before and after exposure to the fuel. These data show no significant differences among the fuels.

To evaluate the compatibility of the semi-synthetic fuel with refuelling hose lining material, samples of used refuelling hose were obtained from the fuel handling facilities at Johannesburg international Airport. Sections of hoses were cut out and soaked in the crude oil-derived jet A-1 and two semi-synthetic fuels with different aromatic concentrations to compare the effects of the fuels on volume swell and mass increase (ASTM D471). The results are presented in Figure 3. Again no significant difference were found between the fuels.

Lubricity

Fuels with low sulphur and low aromatic content are usually considered to have poor lubricity properties. Because of the relatively poor lubricity properties of the synthetic jet fuel component, it was decided to blend crude oil-derived jet fuel from the Natref refinery with the synthetic jet fuel in a 1:1 ratio to ensure adequate lubricity. The BOCLE wear scar diameters (ASTM D5001) for the different fuels are presented in Table 2.

TABLE 2: LUBRICITY OF SASOL FUELS

Fuel	BOCLE WSD[1], mm
Synthetic component	0.90
Natref Jet A-1	0.63
Semi-Synthetic 1 (50/50)	0.68
Semi-Synthetic 2 (75/25)	0.69

Note: 1 WSD = Wear Scar Diameter

In the BOCLE test, a larger number means that the use of the fuel resulted in a larger wear scar diameter during the test and, therefore, has a lower lubricity. Figure 7 shows a histogram of lubricity data from about 1 500 Jet A and Jet A-1 fuels that were sampled worldwide by the U.S. Air Force which puts the lubricity of the semi-synthetic jet fuels into perspective. The BOCLE ratings of the semi-synthetic fuels are only slightly higher than the average of the worldwide values. The semi-synthetic fuels have also been shown to respond well with respect to lubricity to the addition of the corrosion inhibitor, DCI-4A, used in this case as a lubricity improver. This is shown in Figure 6.

Dielectric constant/Density correlation

Boeing measured the dielectric constant of the Sasol fuels. The results compare well with data from the Boeing worldwide survey of Jet A and Jet A-1. The semi-synthetic fuels have density/dielectric characteristics that are typical of conventional fuels and will not cause problems in tank gauging equipment.

Density/temperature correlations

Density measurements were carried out 15, 20, and 40 °C. The results are shown in Table 3. Figure 8 compares the data with density/temperature data from the Boeing world-wide survey of Jet A and Jet A-1 fuels and shows that the density/temperature characteristics of the semi-synthetic fuels and Natref crude oil-derived Jet A-1 are exactly the same as other fuels.

TABLE 3: DENSITY/TEMPERATURE CHARACTERISTICS OF SASOL JET FUELS

Fuel	Fuel density, kg/m^3		
	15 °C	20 °C	40 °C
Natref Jet A-1	800.5	794.7	782.1
SS-1 (50/50)	784.4	780.8	766.1
SS-2 (27/75)	791.6	780.3	773.3

Naphthalenes and other aromatics

The blending of the synthetic and crude oil-derived jet fuels has the effect that the naphthalenes found in the crude oil-derived product are diluted because there are no naphthalenes present in the synthetic jet fuel component. When the synthetic jet fuel component is analyzed by FIA (ASTM

D1319), a small amount of aromatics, in the range of 0.5 to 2 percent, are sometimes detected. Subsequent analysis by supercritical fluid chromatography (ASTM D5186) showed that this was really the tail end of the iso-paraffins and that no aromatics were present. The FIA procedure is not considered accurate for fuels with aromatic concentrations of less than 5 volume percent. The chemical composition of the synthetic jet fuel is given in Table 4.

TABLE 4: CHEMICAL COMPOSITION OF SYNTHETIC JET FUEL

Hydrocarbon type	Mass percent
Monocyclic aromatics	< 0.5
i-Paraffins	96.5
n-Paraffins	3.5

Volatility and Vapour pressure

The volatility of the product is a function of the way in which the product is fractionated. The fractionation can be controlled to give a product with the desired volatility. Results obtained using the Seta Vap vapour pressure apparatus according to ASTM D5191 have shown that the blends are not different from crude oil-derived jet fuel (Table 5).

TABLE 5: VAPOUR PRESSURE

Fuel	Reid vapour pressure, kPa		
	37.8 °C	50 °C	77 °C
Natref Jet A-1	4.1	5.0	8.6
SS-1 (50/50)	3.8	4.4	8.1
SS-2 (75/25)	3.7	4.8	8.5

A boiling point distribution comparison with the 1995 USA Jet A fuel survey is given in Figure 9. From the figure, it is clear that the semi-synthetic jet fuel blends compare favourably with the data obtained from the survey.

Consistency of the product

The processes in use to produce the synthetic jet fuel component are all standard Sasol refining processes. It is important to note that the product is a mature product that Sasol has been making for over 15 years for use both as illuminating kerosene and as a blending component for diesel fuel. The production processes used to produce the synthetic component do not require any further development and all the necessary quality control procedures are already in place.

The final Jet A-1 will be blended at the Natref refinery where the semi-synthetic Jet A-1 will be certified to conform to the requirements of the Joint Checklist. The product will be shipped to the fuel depot at Johannesburg International Airport by dedicated pipeline.

Storage stability

Storage stability is often a concern with hydrotreated fuels because they readily form peroxides and, for this reason, the addition of anti-oxidants is required. Accelerated storage stability tests have been conducted to investigate the gum formation properties of the fuel and to evaluate the effectiveness of an anti-oxidant in preventing peroxide formation.

Accelerated storage stability tests were conducted on the petroleum Jet A-1 from Natref and two semi-synthetic blends, SS-1 (50/50 blend) and SS-2 (75/25 blend). The blends were tested with and without an anti-oxidant and the peroxide concentration in the fuel was measured at various times. The ageing temperature was 65 °C with one week of accelerated storage under these conditions being considered to be equivalent to 16 weeks storage at 21 °C according to ASTM D4625. Table 6 shows the peroxide formation data as a function of time.

The fuel specifications for Jet A-1 do not specify a limit on existing peroxides, however, the fuel specification for JP-5, MIL-T-5624, limits existing peroxides for JP-5 to 8.0 ppm. Using this as a guide, the data presented in Table 6 show that the semi-synthetic blends did form a few ppm more peroxides than the crude oil-derived Jet A-1, but even after 6 weeks at 65 °C, the peroxide levels were still much less than that which is allowed for in the JP-5 specification. The anti-oxidant was effective in preventing the formation of peroxides, although the semi-synthetic blends resisted peroxide formation even without the anti-oxidant.

TABLE 6: PEROXIDE CONCENTRATIONS UNDER ACCELERATED STORAGE CONDITIONS

Fuel	Anti oxidant concentration, mg/ℓ	Peroxide concentration, ppm				
		0 weeks	1 week	2 weeks	3 weeks	6 weeks
Natref	0	0.30	0.80	1.38	1.43	1.45
SS-1	0	1.37	3.88	2.95	2.91	4.17
SS-1	20	0.03	0.77	2.82	2.00	2.14
SS-2	0	0.16	2.23	2.70	2.74	2.58
SS-2	20	0.02	0.95	1.66	1.60	1.32

Potential gum levels (ASTM D873), where the fuel is stored at 100 °C under 800 kPa of oxygen, were also determined on the Natref Jet A-1 and the 50/50 blend, assuming it to be the worst case. Sixteen hours under these conditions is considered equivalent to 40 months at ambient conditions according to ASTM D5304. The results are presented in Table 7.

TABLE 7: POTENTIAL GUM RESULTS

Fuel		Potential Gum, mg/100 ml	
Type	**Sample**	**16 hrs**	**96 hrs**
Natref Jet A-1	1	0.6	2.1
Natref Jet A-1	2	1.3	1.9
SS-1 (50/50)	1	1.9	3.4
SS-1 (50/50)	2	1.9	4.5

Although the gum levels under these accelerated conditions were slightly higher in the case of the semi-synthetic blend they were still much less than the 7.0 mg/100 ml of existent gum (ASTM D381) allowed for in the Jet A-1 fuel specifications. Sasol considers the synthetic component to be a hydrotreated material therefore an anti-oxidant is required by the fuel specifications and will be used at the treat rate of 20 mg/ℓ in the synthetic component. To summarise, the semi-synthetic jet fuel has very good storage stability and does not form excessive amounts of peroxides or gums.

Contaminants

Only trace amounts of contaminates can be found in the synthetic jet fuel component. There are no metals, sulphur, or nitrogen carried over from the original coal gasification process. These are left behind in the condensables with the tars and ash. The carbon monoxide and hydrogen produced by coal gasification are passed over an iron catalyst during the Fisher-Tropsch process. The C_3 and C_4 olefins are then distilled from the synthetic crude by cold separation, so there can be no carry over of contaminants such as iron. The polymerisation process is catalysed using phosphoric acid impregnated in a matrix. The products produced must then be tested for phosphorus carry-over since phosphorus will poison the hydrotreating catalyst used in the next production step. Quality control methods for this potential problem have been in place since Sasol began producing the iso-paraffinic kerosene over 15 years ago.

The Fisher-Tropsch process is known to produce oxygenates, however, these are either removed during the C_3 and C_4 olefin separation or by means of the hydrotreating process. The iso-paraffinic kerosene was analyzed for contaminants including metals and oxygenates (alcohols, acids, phenol, and carbonyls). The analytic methods are summarised in Table 8 and the results are shown in Table 9.

TABLE 8: METHODS USED FOR CONTAMINANT ANALYSES

Analysis	ASTM method or equivalent
Total carbonyls	ASTM E 411/UOP 624
Total alcohols	UOP 656
Esters	SASOL METHOD
Acid number	ASTM D3242
Total phenols	SASOL METHOD
Aromatics	UOP 495
Nitrogen	ASTM D5453
Sulphur	ASTM D5453
Metals	ICP/AAS

TABLE 9: TYPICAL ANALYSES FOR CONTAMINANTS IN THE SASOL SYNTHETIC JET FUEL COMPONENT

Oxygenate	Synthetic jet fuel component	Jet A-1
Carbonyls as MEK, mg/kg	< 25	32
Alcohols as EtOH, wt %	< 0.01	0.05
Esters, mg KOH/g	< 0.001	-
Phenols, mg/kg	1	120
Acid number, mg KOH/g	0.001	0.0002
Sulphur, mg/l	1	2300
Nitrogen, mg/l	1	2
Phosphorus, mg/l	< 0.1	0.4
Iron, ppm	0.1 - 0.5	0.1 - 0.5
Copper, ppm	< 0.01	< 0.01
Lead, ppm	< 0.05	< 0.05

Biocide additive efficacy

A comparison of the efficacy of Biobor JF in the semi synthetic jet fuel and the crude oil-derived jet fuel, was carried out using the MIL-S53021 test method. Biobor JF is the only IATA approved biocide for jet fuel. The microbes used in the biocide evaluation included the following:

- *Candida tropicalis (Yeast)*
- *Pseudomanas aeruginosa (Bacteria)*
- *Hormoconis (Cladosporium) rasinae (Mould)*

The tests were performed at two Biobor JF dosage levels, 135 ppm, the prescribed concentration and 270 ppm, which is the maximum recommended dosage.

The results are expressed as the log of colony forming units per ml of water sample (log cfu/ml). The assumption made in the study is that a change of one log unit or more in micro-organism numbers (cfu/ml) indicates a significant change or effect. The results have shown that Biobor JF is not effective as a biocide in crude oil-derived jet fuel. However, as a biostat Biobor JF is effective as it suppressed regrowth slightly when compared to the control where limited regrowth occurred. In the Semi-Synthetic jet fuel sample tested, the micro-organism growth was similar to that found in the crude oil-derived jet fuel. Biobor JF at the recommended concentration of 135 ppm, was found to be effective in controlling microbial growth.

SUMMARY AND CONCLUSIONS

Sasol proposes to use a synthetic jet fuel component as a blending component to increase the availability of Jet A-1 at Johannesburg International Airport. It will be blended into crude oil-derived Jet A-1 currently produced by Sasol at its Natref crude oil refinery. The resultant semi-synthetic aviation fuel will meet all of the table values and conditions of Defence Standard 91-91 and ASTM D1655 for Jet A-1 fuel.

- The blend will contain a maximum of 50 volume % synthetic jet fuel component.
- The minimum amount of aromatics present in the blend will be 8 volume %.
- All the aromatics present in the blend will come from the crude oil-derived jet fuel.
- The limit on the aromatics will ensure that the blend is compatible with the fuel system elastomers
- The blending of the synthetic jet fuel component with crude oil-derived jet fuel will ensure that the final blend will have adequate lubricity properties.
- It was demonstrated that semi-synthetic Jet A-1 has good storage stability properties.

Sasol synthetic jet fuel is an excellent blending component to blend semi-synthetic Jet A-1.

Acknowledgements

Many people have contributed to this effort either with data or with suggestions and advice. The author wishes to especially thank the Natref laboratory staff who did most of the analytical test work.

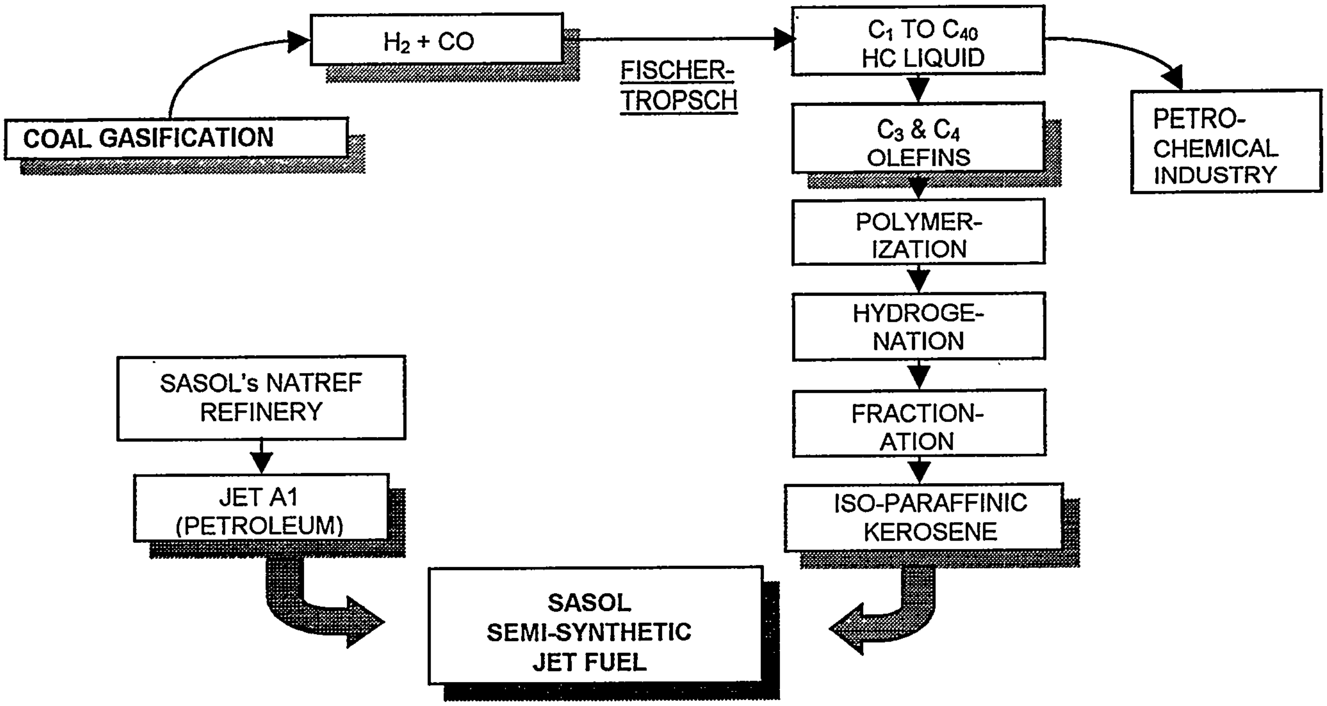

FIGURE 1: PRODUCTION SCHEME FOR SASOL SEMI-SYNTHETIC JET FUEL

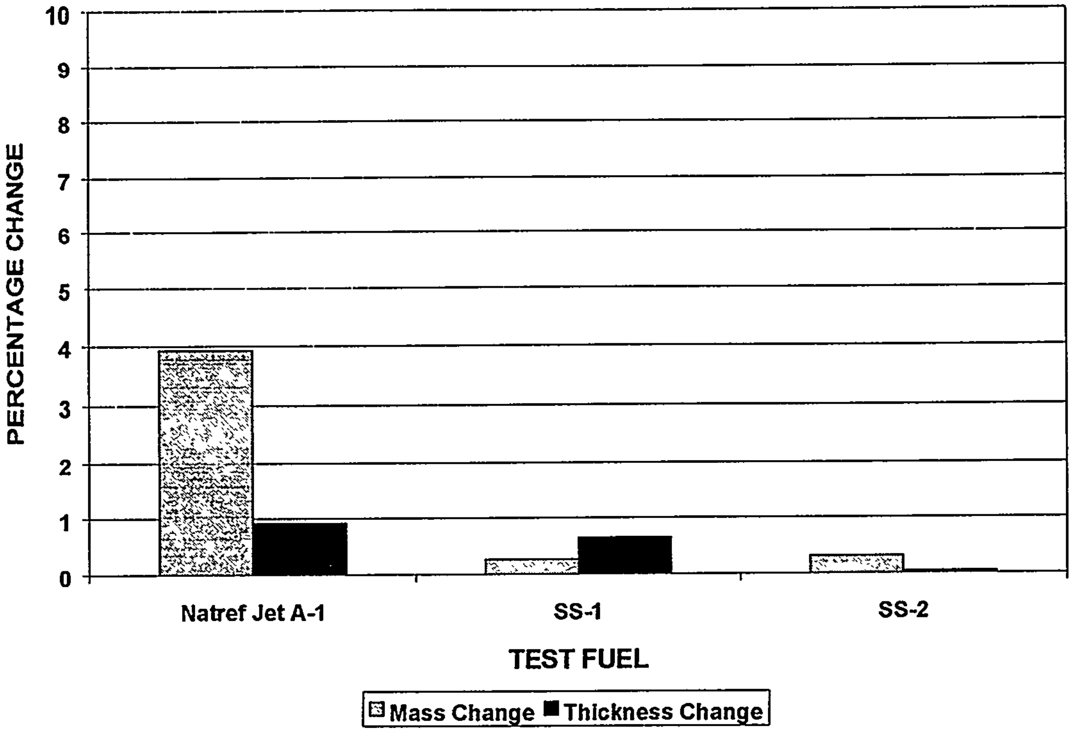

FIGURE 2: MASS AND VOLUME CHANGE FOR VITON

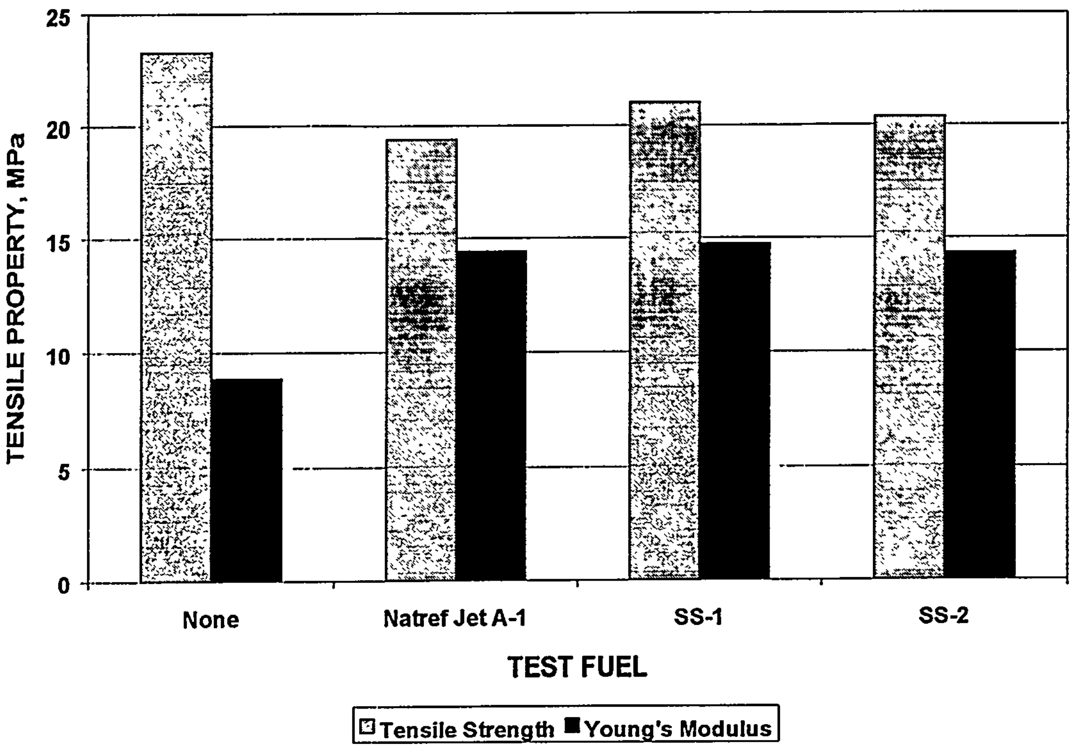

FIGURE 3: VITON STRENGTH RESULTS

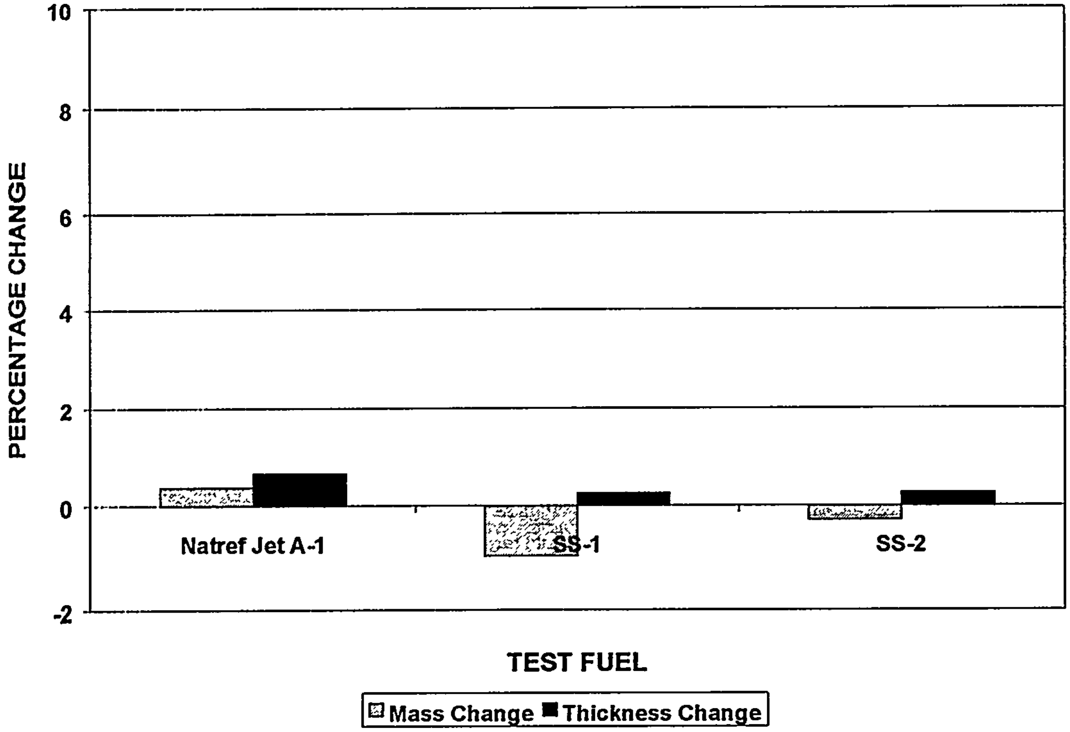

FIGURE 4: MASS AND VOLUME CHANGE FOR BUNA-N

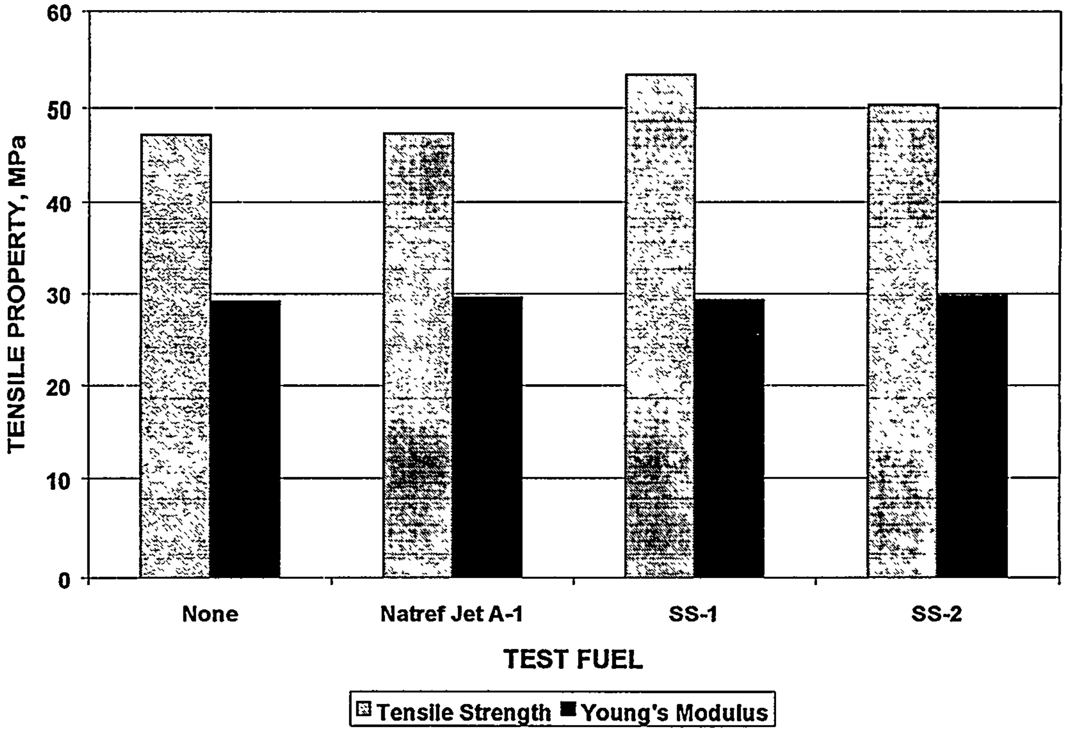

FIGURE 5: BUNA-N STRENGTH RESULTS

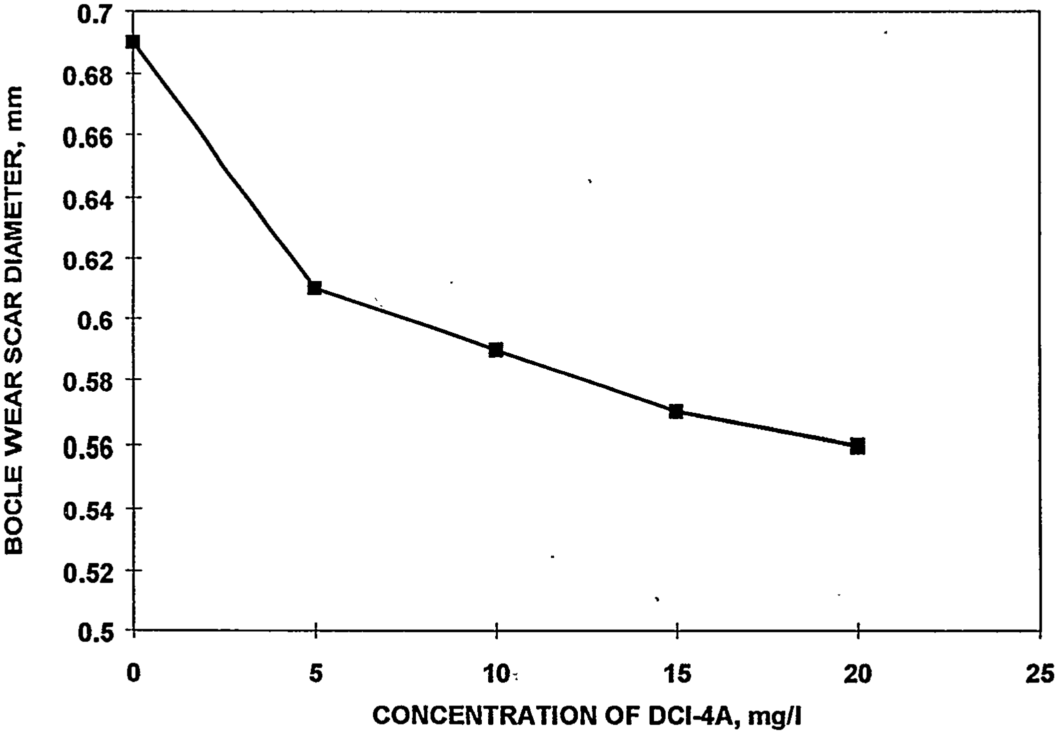

FIGURE 6: RESPONSE OF SASOL SEMI-SYNTHETIC JET FUEL TO THE ADDITION OF DCI-4A

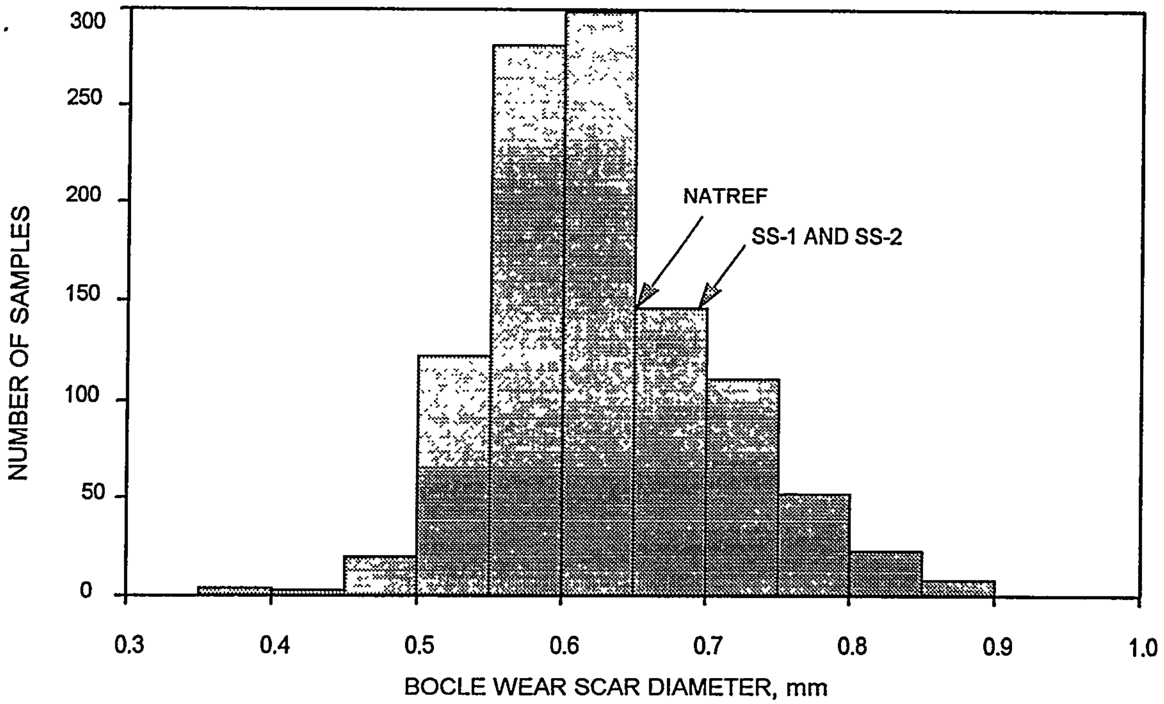

FIGURE 7: HISTOGRAM OF LUBRICITY DATA FOR JET A AND JET A-1

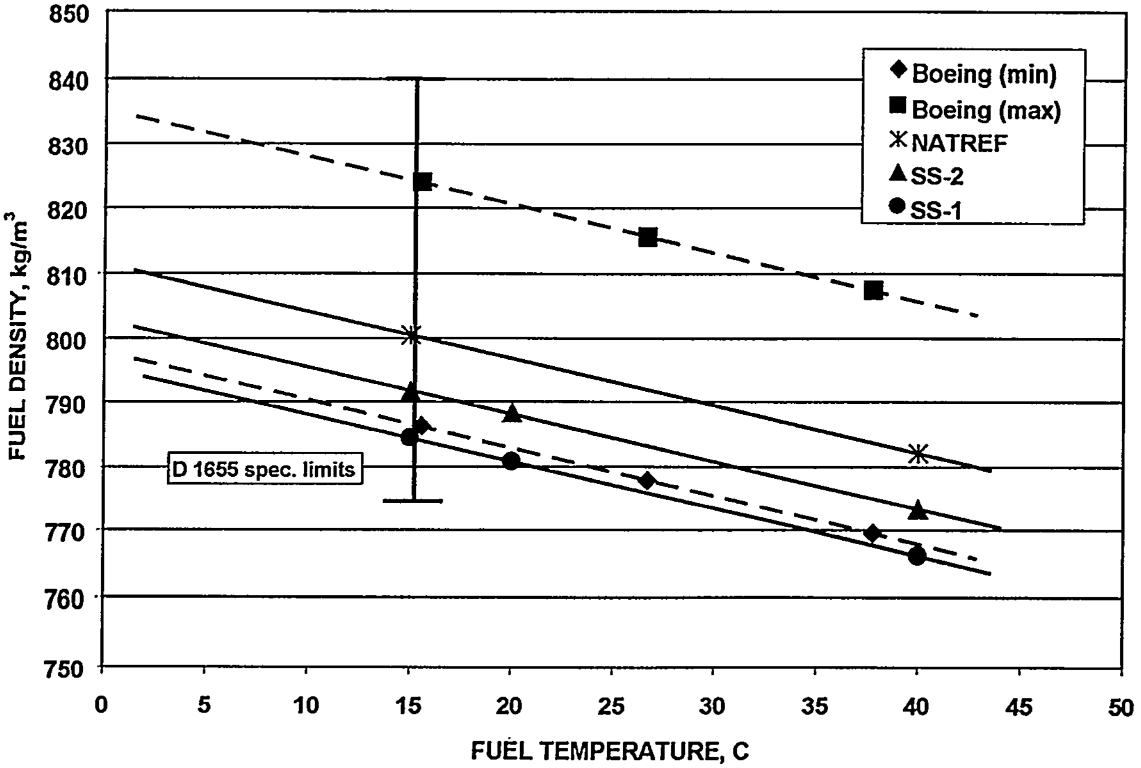

FIGURE 8: DENSITY/TEMPERATURE DATA FROM THE BOEING WORLDWIDE SURVEY OF JET A AND JET A-1

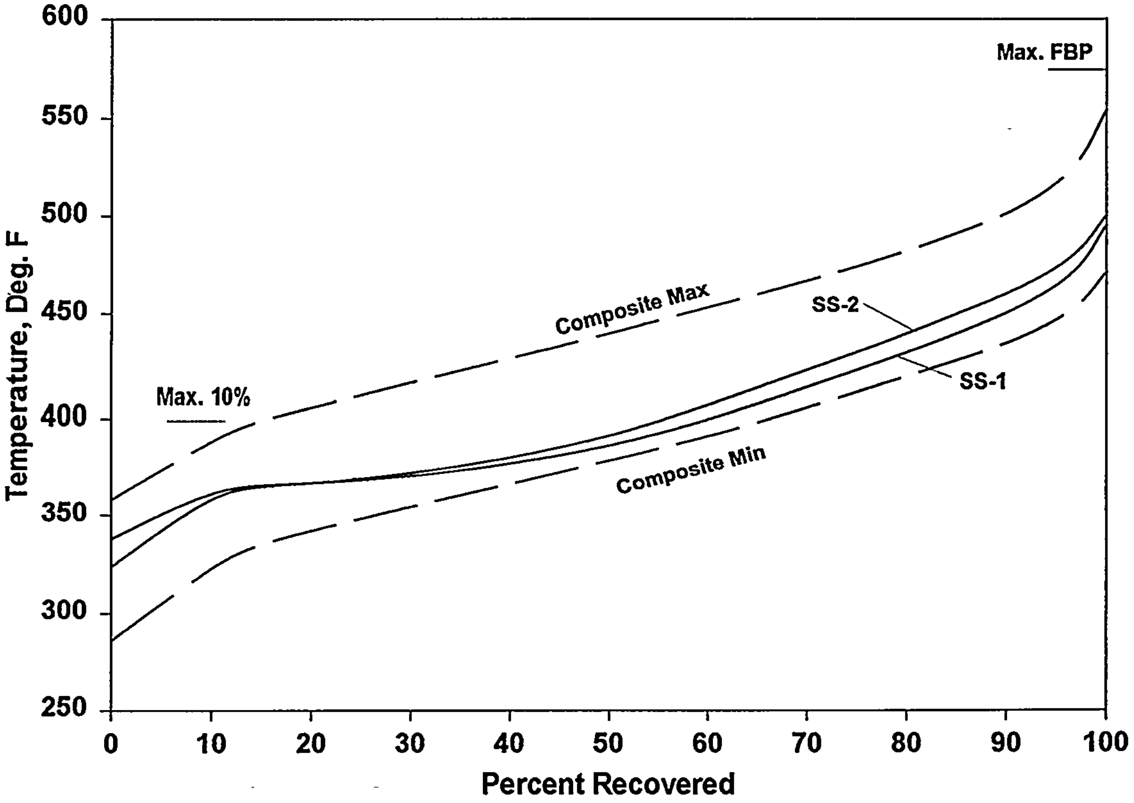

FIGURE 9: BOILING POINT DISTRIBUTION SURVEY OF JET A IN THE USA IN 1995

6th International Conference
on Stability and Handling of Liquid Fuels
Vancouver, B. C., Canada
October 13-17, 1997

EVALUATION OF THE STABILITY, LUBRICITY, AND COLD FLOW PROPERTIES OF BIODIESEL FUEL

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ABSTRACT

The stability, lubricity, and cold flow properties of fuels containing a commercially available methyl soyate biodiesel fuel were evaluated. The stability of the neat biodiesel fuel was significantly inferior to that of a typical, additive-free LS No. 2 diesel fuel. In fuel blends containing varying concentrations of biodiesel, total insolubles formed during ASTM D4625 and ASTM D2274 were greater for blends of intermediate compositions than for either LS FO2 or neat biodiesel. The instability of biodiesel appeared to be primarily due to a peroxidation mechanism similar to that known to occur in fats and oils. Conventional distillate stability additives did not effectively control instability in fuel blends containing biodiesel. A hindered phenol antioxidant was the most effective additive for controlling instability. A phenylene diamine antioxidant was not effective in controlling insolubles formation in fuel blends containing biodiesel, even though other tests indicated that the additive was controlling the peroxidation. The presence of steel significantly decreased the stability of fuels containing biodiesel, and commonly used corrosion inhibitors and metal deactivators made the situation much worse. Biodiesel imparts excellent lubricity to fuel blends that contain as little as 2% of it. Although cold flow properties of biodiesel were inferior to that of a conventional, additive-free LS No. 2 diesel fuel, a typical cold flow improver additive was able to improve CFPP in a fuel blend containing 20% biodiesel. Although higher cold flow improver additive concentrations were required in the 20% biodiesel blend, maximum additive effectiveness in the 20% biodiesel blend was superior to that achieved in the LS FO2. Some information on stability test method reliability is also given.

INTRODUCTION

For many years, various alternatives to petroleum-based distillate fuels have been investigated. During the early 1980's, vegetable oils were studied as possible diesel fuels and diesel fuel extenders.[1-7] However, this work stopped when it became apparent that such fuels caused extremely serious engine deposit problems.[8] More recently, a new vegetable oil-derived material has been investigated. The name most commonly given to such material is "biodiesel."[9] In June, 1994, an ASTM task force was set up to look further at biodiesel fuel. One of its firsts acts was to adopt a definition of biodiesel:[9]

> *Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils and animal fats, for use in compression ignition (diesel) engines.*

The most common biodiesel fuel is made by transesterification of soy or rapeseed triacylglycerides with methanol in the presence of a strong base catalyst such as sodium hydroxide, potassium hydroxide, or sodium methoxide.[10] Methanol also serves as the reaction solvent. The excess of methanol beyond the required stoichiometric amount drives the reaction to essential completion. Unreacted methanol and reaction byproducts such as glycerine are generally removed by water washing. Distillation is another manufacturing step that is sometimes used to provide even higher product purity.[10] The resulting biodiesel fuel is the methyl esters of the mono-carboxylic acids derived from the vegetable oil triacylglycerides.

As a result of further work within the ASTM Biodiesel Task Force, a biodiesel standard has been established as a baseline for further consideration. A copy of this standard is represented in the data found in Table I. The National Biodiesel Board has adopted this standard, and monitors the various commercially available biodiesels to determine which ones meet all of its requirements.[9]

Probably the most widely documented positive attribute of biodiesel fuel is its improved (lowered) emissions when used in conventional diesel engines. Studies generally agree that unburned hydrocarbons (HC) and CO are significantly reduced relative to conventional No. 2 diesel fuel.[11-13] There is less agreement on the effect on particulates and NOx. Some studies show no effect on NOx,[11] while others show an increased level relative to conventional No. 2 diesel fuel.[12-13] Particulates appear to increase in some studies,[13] but decrease in others.[11-12]

Not surprisingly, biodiesel fuel has good lubricity. Blends of biodiesel with conventional No. 2 diesel fuel have also been shown to have improved lubricity compared to the No. 2 diesel fuel alone.[9]

The area of greatest concern regarding biodiesel is fuel stability. Plant-derived fatty acids are well known to be prone to oxidation.[14] The reaction mechanism, the peroxidation chain process, is well understood. The first products of oxidation are hydroperoxides. As they decompose, other products form including acidic species and larger molecular weight materials. Fats and oils that degrade in this way are said to have undergone oxidative rancidity. Several studies have already shown that neat biodiesel as well as blends of biodiesel and conventional No. 2 diesel fuel are prone to such deterioration.[15-16] One study, yet to be published, shows that long term stability of a pure biodiesel fuel was significantly less than that of either conventional No. 1 or No. 2 diesel fuels. Furthermore, there appeared to be a very large antagonism between biodiesel and either No. 1 or No. 2 diesel fuel.[15] Blends of biodiesel and No. 2 gave total insolubles much greater than those observed with either pure biodiesel or No. 2 diesel fuel. A similar trend was noted for blends of biodiesel and No. 1 diesel fuel. Another study indicated that the presence of metals such as steel and copper can increase the instability of pure biodiesel and blends of biodiesel with JP-8, high sulfur (HS) No. 2, and low sulfur (LS) No. 2.[16] High total acid numbers (TAN) and the formation of viscous gum-like material on the metal specimens and on the bottom of the glass test vessels were observed. While copper appeared to promote the most gum formation, iron promoted the highest overall TAN's. Interestingly, the TAN's developed in the biodiesel blends had the following overall ranking, especially when steel was present:

Bio/HS No. 2 << Bio/LS No. 2 <Bio/JP-8

Although not discussed by the authors of that work, this ranking strongly suggests that naturally occurring antioxidants present in the HS No. 2 may help stabilize blends containing that fuel. LS No. 2 and JP-8 would be expected to contain much less of those naturally occurring antioxidants due to the hydrotreating and distillation processes that they respectively experience. It has already been established that LS No. 2 diesel fuel is more prone to oxidation under sufficiently accelerated conditions than HS No. 2 diesel fuel.[17] There is no significant reported work on the ability of conventional antioxidants and distillate stability additives to improve the stability of biodiesel fuel, either in its neat form or when blended with conventional distillate fuels.

Another area of concern for biodiesel fuel is low temperature flow properties. It is already known that pure biodiesel fuel will have inferior cloud and pour points compared to conventional No. 2 diesel fuel.[9,18] At least one study involving actual field use of 80% No. 2 diesel fuel/20% biodiesel fuel blends has reported filter plugging at temperatures near -9°C, although the exact cause was not given.[19] Other field studies indicate low-temperature start-up and operability problems with biodiesel tend to occur when overnight ambient temperatures approach 0°C.[18] The effectiveness of conventional distillate cold flow additives to improve properties such as Cold Filter Plugging Point (CFPP) and Pour Point also needs to be investigated.

The purpose of the work reported in this paper was to further investigate the stability, lubricity, and cold flow properties of a typical, commercially available biodiesel fuel, both in its neat form, and blended at various levels with a conventional additive-free LS No. 2 diesel fuel. Also, the effect of antioxidants, distillate stability additives, corrosion inhibitors, metal deactivators, a multi-functional premium diesel fuel additive, and a cold flow improver additive was evaluated.

EXPERIMENTAL

Fuel Samples

A five-gallon sample of biodiesel fuel was obtained from MARK-IV, L.L.C., and consisted of methyl soyate esters. The sample had been analyzed just prior to shipping to the Amoco Research Center, and an analysis report was sent under separate cover. A copy of the data from that report is given in Table I, and shows that the biodiesel sample complied with all the requirements of the National Biodiesel Board standard. The biodiesel fuel sample was used without any further processing. When not being used, the biodiesel sample was stored at 40°F in its original sealed container.

A ten-gallon sample of a refinery-fresh low sulfur No. 2 diesel fuel (LS FO2) was obtained. Care was taken to insure that the LS FO2 contained no additives. The LS FO2 was tested for typical properties, and results are given in Table II. When not being used, the LS FO2 was stored at 40°F in its original sealed containers.

Six additive-free fuel blends were made from the LS FO2 and the biodiesel for much of the test work. The concentration of biodiesel in those six blends were 0, 2, 10, 20, 50, and 100%(vol). The 0% biodiesel fuel blend was simply the LS FO2; the 100% biodiesel blend was the neat biodiesel.

Additives

The effect of selected additives were determined for certain fuel blends. Information concerning the additives and the concentrations at which they were used are given below:

Designation	Structural information	Function	Concentration, ppm
Additive A	N,N'-di-sec-butyl-p-phenylene diamine	antioxidant	50
Additive B	2,6-di-t-butyl-4-methylphenol	antioxidant	50
Additive C	N,N-dimethylcyclohexylamine	stabilizer	20
Additive D	Basic nitrogen, proprietary	stabilizer	20
Additive E	N,N'-disalicylidene-1,2-propanediamine	metal deactivator	20
Additive F	Proprietary	metal deactivator	20
Additive G	Dimer acid	corrosion inhibitor	20
Additive H	Non-acidic, proprietary	corrosion inhibitor	20
Additive I	Proprietary	multi-functional premium diesel	450
Additive J	Proprietary	cold flow improver	various

Additives A, B, C, and H were essentially 100% active; the others contained varying levels of diluents. All additives were commercially available and used as received. The effect of additives A-D and J were measured on an 80% LS FO2/20% biodiesel blend; the effect of additives E-I were measured on a 50% LS FO2/50% biodiesel blend.

Tests

Initial tests performed on the biodiesel fuel and LS FO2 are given in Tables I and II, respectively. The various fuels and fuel blends with and without additives were tested for stability, lubricity, and cold flow properties using the following procedures:

Stability:

Oxidative Stability (ASTM D2274)
Nalco Pad Stability
Storage Stability (ASTM D4625)
40-Hour Stability
40-Hour Stability with Steel Specimen
Initial Peroxide Number (ASTM D3703)
Peroxide Number After D4625 (ASTM D3703)
Peroxide Number After D2274 (ASTM D3703)
Peroxide Number After Nalco Pad (ASTM D3703)
Hydroperoxide Potential, CRC Procedure
TAN (ASTM D664)

Lubricity:

Scuffing BOCLE
High Frequency Reciprocating Rig (HFRR)

Cold Flow:

Cloud Point (ASTM D2500)
Pour Pount (ASTM D97)
CFPP (IP 309)

The ASTM procedures are well documented and will not be described further here. The Nalco Pad stability procedure measures thermal stability and has been described elsewhere.[20] ASTM D2274 and the Nalco Pad test are known not to correlate with real storage stability. However, they were included since they continue to be used as specification tests by many diesel fuel marketers and customers. The 40-Hour Stability test is a procedure developed and used by Amoco Oil Company. Over ten years of use and hundreds of No. 2 distillate fuel samples have shown this procedure to correlate well with the reliable ASTM D4625. Details of this procedure are documented elsewhere.[24] The CRC Hydroperoxide Potential procedure was originally developed for jet fuels[21] and involves heating a 100 ml fuel sample at 65 C and 1 atmosphere air for four weeks. Peroxide Number is then determined as an indication of the fuel's hydroperoxide susceptibility. TAN was measured after many of the stability tests as yet another measure of the progress of oxidative deterioration experienced by the fuels. The lubricity test procedures are well known and will not be discussed further here. Work to determine the effect of metals on fuel stability was limited to steel, since steel is by far the most common metal that diesel fuels contact. To measure the effect of steel on fuel stability, the 40-Hour test was chosen, due to its relatively short storage time and its prior record as a reliable predictor. The test was run with and without a steel strip so as to measure the effect of steel on stability. The steel strips were SAE 1010 CR 1" by 3" by 1/16" polished 280 grit with a 1/8" hanging hole. They were obtained from Metaspec, in San Antonio, Texas. Each steel strip was removed from the clear plastic, form-fitting package just prior to use. Other than soaking and repeated rinsing in reagent-grade N-heptane to remove a protective oil coating (as recommended by the manufacturer), the steel strips were used as received. When used, a steel strip was completely immersed in the fuel sample and allowed to freely lean on the side of the bottom of the glass tube. Then the 40-Hour test was run as usual. The Cold Filter Plugging Point (CFPP) test is well established, and is widely used in the U.S. and Europe to estimate low temperature operability of No. 2 diesel fuel.[22]

RESULTS AND DISCUSSION

Stability

General stability results for the six additive-free fuel blends are given in Table III and Figure 1. The ASTM D4625 test was run in duplicate for the six additive-free blends. Only average values are reported. However, individual replicate values never differed by more than 0.20 mg/100 ml. Biodiesel had inferior stability compared to the LS FO2, as indicated by the D4625 test results. Also, as the concentration of biodiesel in the fuel blends increased, the destabilizing effect of biodiesel was apparent. However, the instability as evidenced by the insolubles generated did not continually increase as biodiesel content increased from 0% to 100%. Instead, insolubles peaked near the 10% biodiesel blend. However, the amount of peroxidation that occurred as indicated by the TAN's after D4625 appeared to continually increase as the concentration of biodiesel increased. One possible reason for the insolubles not continuing to increase even though peroxidation continues to increase is that the instability reaction products are more soluble (up to a point) in the fuel blends that contain higher levels of biodiesel.

Directionally, D2274 data tracked similarly to that of D4625. However, the peak insoluble values observed in the D2274 data were much greater than those for D4625. Also, D2274 is known to generally underestimate real world storage stability for conventional No. 2 diesel fuel.[27] However, for the fuel blends with 20% or more of biodiesel, D2274 gave insoluble levels that were greater than D4625. A probable reason for this is the much more highly oxidative environment of D2274 compared to D4625. Since fuels containing biodiesel are much more prone to peroxidation than conventional LS No. 2 diesel fuel, the test conditions of D2274 may exaggerate the instability of biodiesel blends. The generally higher TAN values measured after D2274 relative to those measured after D4625 also indicated that more peroxidation occurred during the D2274 test conditions.

The peroxide number and TAN values measured after the CRC Hydroperoxide Potential test also indicate the differences in how biodiesel blends and conventional LS No. 2 diesel fuel oxidize. The neat biodiesel and the biodiesel blends all had final peroxide numbers less than that of the LS FO2. However, the TAN's increased continually from neat LS FO2 to neat biodiesel. Apparently, the hydroperoxides formed in LS FO2 did not decompose in the same way as did those formed when biodiesel is present. The higher TAN of the biodiesel blends indicate more peroxidation final products in those fuels. The long test time (4 weeks), temperature (65 C), and the limited oxygen availability (compared to other tests), may have caused the hydroperoxides in the biodiesel-containing fuels to decompose more completely during the CRC procedure.

The Nalco Pad test did not indicate any significant instability in any of the fuels tested, based on the pad rating. However, gum formation in the test glassware and somewhat increasing TAN's for blends with 10% or more biodiesel were observed. This indicates some hydroperoxide decomposition was occurring. Significant color degradation was not observed in any of the fuels during any of the tests.

Effect of Additives on Fuel Stability

Evaluation of the effect of antioxidants and distillate stabilizers on fuel stability was restricted to the 80% LS FO2/20% biodiesel blend. Test results are given in Table IV and Figures 2-3. Looking first at the D4625 test, only the hindered phenol antioxidant, Additive B, had a large beneficial effect on stability as indicated by insolubles. The two distillate stabilizers, Additives C and D did not reduce insolubles very much. However, a more complete understanding of the effect of these additives in the D4625 test is obtained by inspecting the peroxide numbers and TAN's measured after the test. Although the phenylene diamine (PDA) antioxidant, Additive A, was not effective in reducing D4625 insolubles, it did appear to do a good job of controlling the peroxidation process. In fact, the peroxide numbers and TAN's after D4625 indicate that Additive A did a better job than Additive B in controlling peroxidation. This is consistent with previous work showing that PDA's are better antioxidants than hindered phenols.[14] Why then did Additive A not control the amount of insolubles generated during D4625? It has been known for some time that PDA antioxidants increase sediment formation in HS FO2.[23] A recent study showed a similar effect in LS FO2.[24] It may be that the peroxidation control provided by Additive A in the 80% LS FO2/20% biodiesel blend may have been largely offset by an antagonistic affect that generated more insolubles similar to what is known to occur in 100% LS FO2. Although Additive C did not control hydroperoxide or insolubles formation, it did hold the TAN to a level near that of the fuel blend with antioxidant Additives A and B. Since the basicity of the 20 ppm(wt) of Additive C was only 0.008 mg KOH/g, simple neutralization will not explain this. Without further data, it can only be conjectured that Additive C interfered with the way hydroperoxides decompose to form fuel-soluble compounds.

D2274 data gave a picture similar to D4625 in several ways. Both antioxidants did a much better job of controlling peroxidation and the resulting insolubles formation than did the two distillate stabilizers. The insolubles, peroxide numbers, and TAN's measured after D2274 verify those test conditions to be much more oxidatively severe than the D4625 conditions. Under these much more oxidatively severe conditions, Additive C was no longer able to control TAN in the fuel blend. As with the D4625 data, there did not appear to be an advantage to using a combination of hindered phenol and distillate stabilizer over using just the hindered phenol. However, Additive A did a much better job in reducing insolubles in D2274 compared to D4625. If the poor performance of Additive A in the D4625 test was due to the PDA reacting with the LS FO2 component of the fuel blend to form increased insolubles (as discussed earlier), then one would expect D2274 results to be better for that additive. This is because it has been established that the harmful effect of PDA antioxidants is not detected by highly accelerated tests such as D2274.[24] One possible explanation for this is that the much more oxidative environment of D2274 interferes with the PDA sediment forming mechanism. Further work is required to verify this.

The CRC Hydroperoxide Potential data is interesting. All four additives appeared to do a roughly equivalent job in controlling hydroperoxide formation during this test. This does not agree with most of the other data concerning additive performance. One possible explanation is that the conditions of this test procedure favor hydroperoxide decomposition over hydroperoxide formation. This notion is also consistent with the CRC Hydroperoxide Potential data discussed in the previous section.

Nalco Pad tests results did not show much difference between the samples. While hydroperoxide and TAN values were similar among all the fuels, not much was generated in terms of insolubles.

Effect of Steel on Stability

Test results concerning the effect of steel on the stability of the six additive-free fuel blends are given in Table V and Figures 4-5. Generally, the presence of the steel strip decreased fuel stability, as indicated by the 40-Hour insoluble levels. For fuel blends containing 20% or more biodiesel, the appearance of the insolubles was different when steel was present. Although the filters were not analyzed, the insolubles contained very noticeable amounts of a red-orange gritty solid, strongly suggesting that iron salts had formed and then fallen from the steel strip during the test. Also, a coating of a gum-like substance was noted on the filters of the 20% and 50% biodiesel blends when the steel strip was present. The gum-like material was most obvious around the edge of the filter, and it actually made the filter appear translucent. This behavior occurred only with the 50% biodiesel blend when the steel strip was not present, and it was not as pronounced. Steel also appeared to cause some color degradation in fuel blends containing 10% or more biodiesel. A generally increasing trend of corrosion and gum formation on the steel strip was observed as the concentration of biodiesel in the fuel blend increased (Figure 5). Apparently, under the conditions of the 40-Hour Stability test the oxidative instability of the biodiesel is catalyzed by the steel surface. This is not surprising, since the catalytic effect of metals, especially multi-valent transition metals is well known.[28]

The 40-Hour Stability test results when steel is not present (Table V) did not track the same as the D4625 test results from the same six blends (Table III). Therefore, future work using the much less accelerated D4625 with and without steel may be needed to verify the results. However, the harmful effect of steel on biodiesel fuel blend stability under similar mild conditions has been reported elsewhere.[16] It is likely that the qualitative effect of steel as given here is correct.

The effect of several corrosion inhibitors, metal deactivators, and one multi-functional premium diesel fuel additive on fuel stability in the presence of steel was determined. This evaluation was restricted to the 50% LS FO2/50% biodiesel fuel blend. Test results are given in Table VI and Figure 6. None of the additives improved fuel stability. In fact, just the opposite appeared to be true. Insolubles increased for four of the fuel blends relative to the additive free fuel blend. For the fuel blend containing Additive A, a large amount of gum formed, and it degraded the filter to the point that a final weighing was not possible. In general the amount and frequency of gum formation in the five additized fuel blends (Table VI) was greater than what was observed in the six additive-free fuel blends (Table V). The huge amount of gum formed in the Additive G blend is noteworthy, since this was the only additive that was decidedly acidic. It is generally accepted that the organic acids formed from the decomposition of hydroperoxides continue to react to form various insoluble material, including gums.[25] The addition of organic acids to the fresh fuel likely aggravated the situation. None of the additives protected the steel surface from corrosion. Instead, all additives caused increased corrosion and gum formation on the steel surface (Figure 6). This information is particularly disturbing since Additives E-H and others similar to them are virtually always present in fungible LS FO2. Any biodiesel fuel blend that is made for commercial use will likely have such additives present. The long-term effects of such additives on fuel stability and diesel equipment needs to be further investigated.

Lubricity

Scuffing BOCLE and HFRR test results for the six additive-free fuel blends are given in Table VII. Results indicate that biodiesel fuel enhanced the performance of the fuel blends that contained it.. The beneficial effect of biodiesel was most apparent in the HFRR test results, where only 2% biodiesel reduced the wear scar by 70%. Although HFRR results remained quite acceptable for the other biodiesel-containing blends, there did appear to be a decrease in performance as the biodiesel concentration increased. It cannot be determined just from this data if that trend is real or merely test variance. The beneficial effect of biodiesel on Scuffing BOCLE performance was less obvious due the excellent performance of the additive-free LS FO2. Comparing the Scuffing BOCLE and HFRR data for the LS FO2, it is apparent that the two test methods do not always agree, a fact already documented elsewhere.[26]

Cold Flow Properties

The Cloud Point, Pour Point, and CFPP of the six additive-free fuel blends are given in Figure 7. As expected, biodiesel increased (worsened) the Cloud and Pour Points. The CFPP data is more interesting. Generally, CFPP of additive-free conventional No. 2 diesel fuel will be at or just below the Cloud Point. Indeed, this is exactly what was observed for the LS FO2 sample. However, for fuel blends with 10% or more biodiesel fuel, the CFPP was below the Pour Point. These results were checked, and they appear to be valid. One possible explanation is that the methyl esters in sufficient concentration provide just a slight amount of delay to fuel gelling under the dynamic conditions of the CFPP test.

The effect of a typical, commercial cold flow improver additive on fuel cold flow properties was determined. This evaluation was restricted to the LS FO2 and the 80% LS FO2/20% biodiesel fuel blend. Test results are given in Tables VIII and IX. The best indication of cold flow additive performance when using the CFPP test is to determine the amount of CFPP depression below the Cloud Point. Results indicate that the cold flow additive, Additive J, actually gave a superior maximum benefit in the 80%/20% blend compared to the neat LS FO2. However, it took nearly twice as much concentration of Additive J in the 80%/20% blend to reach that level of CFPP reduction compared to the concentration needed in the neat LS FO2. In other words, Additive J achieved its maximum benefit at a lower concentration in the neat LS FO2. However, at higher concentrations, Additive J gave better results in the 80%/20% blend.

CONCLUSIONS

The work reported in this paper supports the following conclusions:

1. The stability of biodiesel is significantly inferior to that of typical LS FO2. Stability as measured by insolubles formation of fuel blends containing biodiesel may be less than either LS FO2 or neat biodiesel.

2. The instability of biodiesel appears to be a peroxidation mechanism similar to that known to occur in fats and oils.

3. Highly accelerated oxidative test methods such as ASTM D2274 will detect instability in fuel blends containing biodiesel. However, the results of such methods may be exaggerated compared to more reliable methods such as ASTM D4625. Test methods such as the Nalco Pad test that rely primarily on thermal stressing do not adequately detect instability in fuel blends containing biodiesel.

4. Conventional distillate stabilizers that rely entirely on basic nitrogen chemistry do not control biodiesel instability.

5. Hindered phenol antioxidants provide significant, but not complete, effectiveness in controlling biodiesel instability. PDA antioxidants do not provide significant effectiveness in controlling insolubles formation in fuel blends containing biodiesel, even though other tests indicate that peroxidation is being controlled. This may be due to an antagonistic effect of PDA on the stability of the LS FO2 component of the fuel blend.

6. Steel surfaces catalyze the oxidative instability of fuel blends containing biodiesel. Commonly used corrosion inhibitors and metal deactivators appear to further antagonize this deleterious effect instead of mitigating it.

7. Biodiesel fuel imparts excellent lubricity to fuels that contain it, even when present at 2%.

8. Cold flow properties of biodiesel can be worse than LS FO2, but conventional cold flow improver additive technology can restore those properties, as measured by CFPP. Although higher additive concentrations (and cost) are required, maximum additive effectiveness in some biodiesel fuel blends can be superior to that achieved in LS FO2.

ACKNOWLEDGMENTS

The contributions of the following people are gratefully acknowledged: Steve Howell, MARK-IV, L.L.C., for providing the biodiesel sample and the corresponding inspection test data; Darlene Smith for making the fuel blends, running tests, and keeping track of the volumes of generated data; Helen Johnson for running much of the stability tests; Debbie Thomas for running all the Peroxide Number and TAN tests; Len J. Gursky, Paramins, for running the HFRR tests; Dave Larson for preparing the bar chart figures; Don Box for photographing the steel strips and preparing the corresponding figures; and Judy Grutsch and Mardy Lamski for formatting the manuscript, and assembling text, tables, and figures into their final eye-pleasing form.

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TABLE I

BIODIESEL INSPECTION PROPERTIES

TEST	METHOD (1)	VALUE	SPEC (2)
Flash point, °C	D93	159	100, min.
Carbon Residue, %(wt)	D189	0.02	0.050, max.
Water and Sediment, %(vol)	D1796	0	0.050, max.
Sulfated Ash, %(wt)	D874	0.003	0.020, max.
Sulfur, %(wt)	D2622	0	0.05, max.
Kinematic Viscosity @ 40°C, cSt	D445	3.685	1.9 - 6.0
Cloud Point, °C	D2500	2	---------
Copper Corrosion	D130	1B	3, max.
TAN, mg KOH/g	D664	0.46	0.80, max.
Peroxide Number, meq O/kg	D3703	3.25	---------
Cetane Number	D613	44.6	40, min.
Glycerin-derived impurities, %(wt)	GC(3)		
Glycerin		0.015	0.020, max.
Mono-glycerides		0.479	------
Di-glycerides		0.151	------
Tri-glycerides		0.120	------
Total glycerides		0.174	0.240, max.

(1) Methods are ASTM unless otherwise noted.
(2) As adopted by National Biodiesel Board.
(3) Gas Chromatograph method as modified from U. S. Dept. of Agriculture.

TABLE II

FUNGIBLE-GRADE LS FO2 INSPECTION PROPERTIES

TEST	VALUE	TEST	VALUE
API Gravity	34.04	Distillation, °C:	
Specific Gravity	0.8548	IBP	187.6
Flash Point, °C	79	10%	217.7
Total Sulfur, %(wt)	0.0261	20%	231.4
Total Nitrogen, ppm(wt)	42	30%	242.0
Basic Nitrogen, ppm(wt)	10	40%	252.6
Color	L0.5	50%	261.8
Karl Fischer Water, ppm(wt)	35	60%	271.2
Composition by Mass Spectrometry, %(wt)		70%	282.0
Paraffins	29.8	80%	295.1
Naphthenes	33.0	90%	313.6
Aromatics	37.2	95%	329.7
Cloud Point, °C	-16.7	FBP	341.6
Pour Point, °C	-20.6		
CFPP,(1) °C	-17.0		

(1) Cold Filter Plugging Point.

TABLE III

STABILITY OF LS FO2 / BIODIESEL BLENDS

% (Vol) BIODIESEL	0	2	10	20	50	100
Stability, D4625(2)						
Total Insolubles, mg/100 ml	0.70	1.50	13.20	2.45	3.70	6.50
Final Color, ASTM	L0.5	L0.5	L1.0	L0.5	L1.0	1.0
Stability, D2274						
Total Insolubles, mg/100 ml	0.3	0.5	7.4	38.2	13.2	12.4
Final Color, ASTM	L0.5	L0.5	1.5	1.5	L1.0	1.0
Nalco Pad Rating	1	1	1	1	1	1
Comments			gum on btm of tube	gum on btm of tube		sm gum on btm tube
Peroxide Number, meq O/kg	<1	2.6	9.8	10.8	15.1	33.9
Hydroperoxide Potential, CRC,(1) meq O/kg	90	19.6	14.4	35.9	66.3	56
Total Acid Number, mg KOH/g						
Initial	<0.01	<0.01	0.20	0.40	0.23	0.69
After D4625	.02	0.11	0.85	1.05	1.27	1.68
After D2274	<0.01	0.03	2.32	4.89	4.72	0.45
After Nalco Pad	<0.01	0.02	0.01	0.10	0.23	0.43
After CRC Hydroperoxide Potential	1.70	2.29	3.19	4.50	5.08	4.76

(1) See EXPERIMENTAL section for a description of this test.
(2) Results are the average of two replicate determinations.

TABLE IV

EFFECT OF ADDITIVES ON THE STABILITY OF AN 80/20 LS FO2/BIODIESEL BLEND

	NO ADDITIVE					
Additive A,(1) ppm(wt)		50	---	---	---	---
Additive B,(2) ppm(wt)		---	50	---	---	50
Additive C,(3) ppm(wt)		---	---	20	---	---
Additive D,(4) ppm(wt)		---	---	---	20	20
Stability, D4625						
Total Insolubles, mg/100 ml	2.45	2.00	1.00	1.80	3.10	1.30
Final Color, ASTM	L0.5	0.5	L0.5	0.5	0.5	L0.5
Stability, D2274						
Total Insolubles, mg/100 ml	38.2	0.50	0.40	33.70	44.10	0.90
Final Color, ASTM	1.5	L1.0	L0.5	L1.5	L1.5	L0.5
Nalco Pad Rating	1	1	1	1	1	1
Peroxide Number, meq O/kg	10.8	----	-----	----	----	----
Peroxide Number after D4625, meq O/kg	----	3.5	89.5	217	262	115
Hydroperoxide Potential, CRC, (5) meq O/kg	35.9	18.8	19.6	12.9	11.1	12.1
Peroxide Number after Nalco Pad, meq O/kg	----	16.9	20.5	20.5	20.9	19.8
Peroxide Number after D2274, meq O/kg	----	61	47.3	775	793	295
Total Acid Number, mg KOH/g						
Initial	0.40	----	-----	----	----	-----
After D4625	1.05	0.12	0.23	0.34	1.00	1.18
After D2274	4.89	0.16	0.13	5.47	4.97	0.43
After Nalco Pad	0.10	0.14	0.15	0.14	0.13	0.12

(1) N,N'-di-sec-butyl-p-phenylene diamine
(2) 2, 6-di-t-butyl-4-methylphenol
(3) N,N-dimethylcyclohexylamine
(4) Proprietary basic nitrogen-containing compound.
(5) See EXPERIMENTAL section for a description of this test

TABLE V

EFFECT OF STEEL ON THE STABILITY OF LS FO2/BIODIESEL BLENDS

%(Vol) BIODIESEL	**0**	**2**	**10**	**20**	**50**	**100**
40-Hour Stability(1)						
Total Insolubles, mg/100 ml	0.10	2.90	0.70	0.80	14.3	13.3
Final Color, ASTM	L0.5	L0.5	L0.5	L0.5	L1.5	L0.5
Comments						
Filter Gums					lt gum	
40-Hour Stability with Steel(1)						
Total Insolubles, mg/100 ml	0.14	3.4	11.3	24.0	23.6	10.9
Final Color, ASTM	L0.5	L0.5	L1.5	L2.5	L3.0	L1.0
Comments						
Filter				heavy rust-like	heavy rust-like	lg. chunks rust -like
Gums				around edge	around edge	
Steel	no change	light varnish	corrosion on edge	corrosion on edge/ hvy gum	corrosion on edge/ hvy gum	corrosion on edge/ mod. gum

(1) See EXPERIMENTAL section for a description of this test.

TABLE VI

EFFECT OF ADDITIVES ON THE STABILITY OF A 50/50 LS FO2/BIODIESEL BLEND WITH STEEL

	NO ADDITIVE					
Additive E,(1) ppm(wt)	----	20	----	----	----	----
Additive F,(2) ppm(wt)	----	----	20	----	----	----
Additive G,(3) ppm(wt)	----	----	----	20	----	----
Additive H,(4) ppm(wt)	----	----	----	----	20	----
Additive I,(5) ppm(wt)	----	----	----	----	----	450
40-Hour Stability with Steel(6)						
Total Insolubles	23.6	----	39.10	302.0	34.10	38.20
Final Color, ASTM	L3.0	L3.0	L3.0	L3.0	L3.0	2.5
Comments						
Filter Particulates	Heavy rust-like		Heavy rust-like		Heavy rust-like	Medium rust-like
Filter Gums	None	Heavy	Very Light around edge	Very Heavy	Very Light	Moderate around edge
Steel	Light corrosion on edge	Very Heavy corrosion & gum	Heavy corrosion & gum	Very Heavy corrosion & gum	Heavy corrosion & gum	Heavy corrosion & gum

(1) N,N'-disalicylidene-1,2-propane diamine
(2) Proprietary metal deactivator
(3) Dimer acid corrosion inhibitor
(4) Proprietary, non-acid corrosion inhibitor
(5) Proprietary, multi-functional premium diesel fuel additive
(6) See EXPERIMENTAL section for a description of this test

TABLE VII

LUBRICITY OF LS FO2/BIODIESEL BLENDS

% (Vol) Biodiesel	0	2	10	20	50	100
Scuffing BOCLE, pass load, g	4,600	>4,700	>4,700	>4,700	>4,700	>4,700
HFRR @ 60°C, microns	571	168	235	381	382	224

TABLE VIII

EFFECT OF COLD FLOW ADDITIVE ON LS FO2

ADDITIVE J, RC⁽²⁾	0	1	2	3	4	5	6
CLOUD C	-16.7	-13.0	-15.0	-14.0	-18.0	-15.0	-15.0
POUR C	-20.6	-34.4	-45.6	-45.6	-51.1	-51.1	-51.1
CFPP⁽¹⁾ C	-17.0	-26.0	-30.0	-33.0	-34.0	-32.0	-33.0
CLOUD-CFPP, C	0.3	13	15	19	16	17	18

(1) Cold Filter Plugging Point
(2) Relative Concentration

TABLE IX

EFFECT OF COLD FLOW ADDITIVE ON 80/20 FO2/LS BIODIESEL BLEND

ADDITIVE J, RC⁽²⁾	0	1	2	3	4	5	6
CLOUD C	-11.6	-10.0	-9.0	-10.0	-9.8	-10.0	-10.0
POUR C	-15.0	-28.9	-40.0	-42.8	-42.8	-42.8	-51.1
CFPP C⁽¹⁾	-18.0	-18.0	-20.0	-26.0	-35.0	-33.0	-33.0
CLOUD-CFPP, C	6.4	8	11	16	25.2	23	23

(1) Cold Filter Plugging Point
(2) Relative Concentration

Figure 1

Stability of LS FO2/Biodiesel Blends

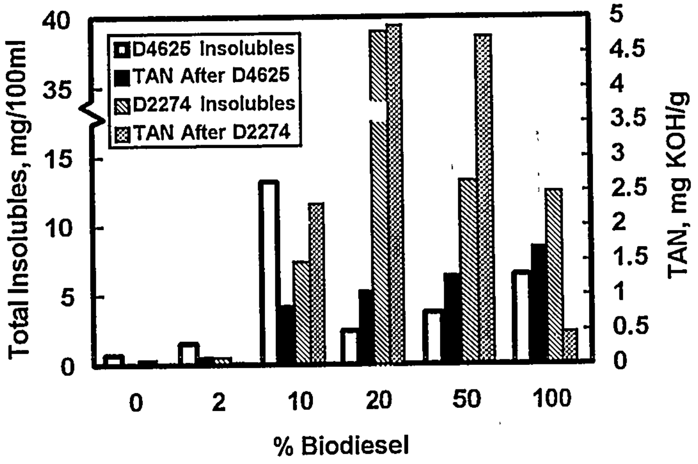


Figure 2

Effect of Additives on ASTM D4625 for an 80% LS FO2/20% Biodiesel Blend

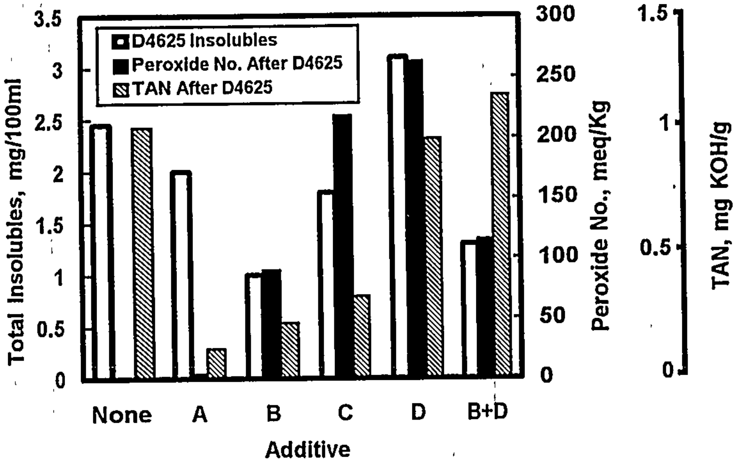


Figure 3

Effect of Additives on ASTM D2274 for an 80% LS FO2/20% Biodiesel Blend

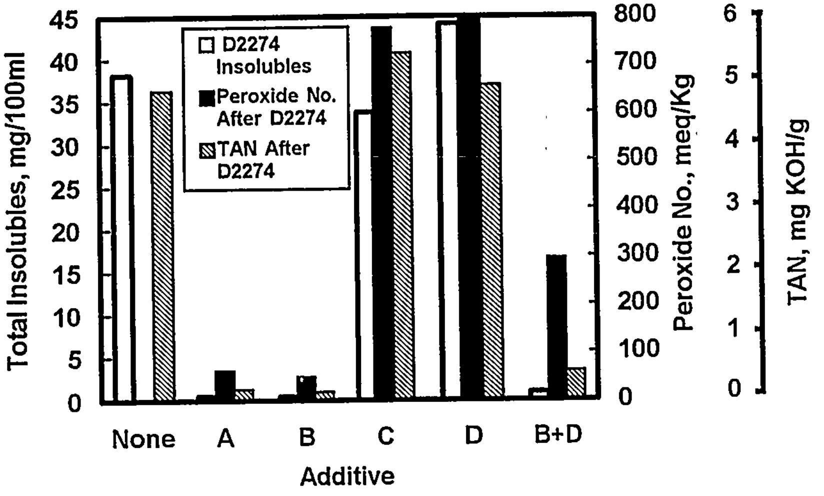


Figure 4

Effect of Steel on the Stability of LS FO2/ Biodiesel Blends

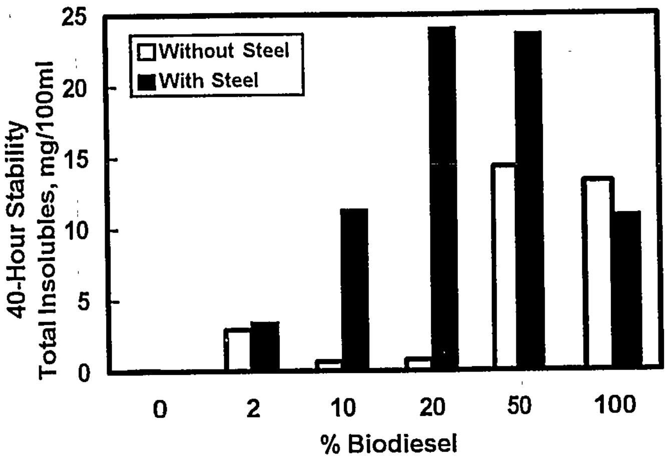


Figure 5

40 - Hour Stability with Steel Strip
Effect of Fuel Composition

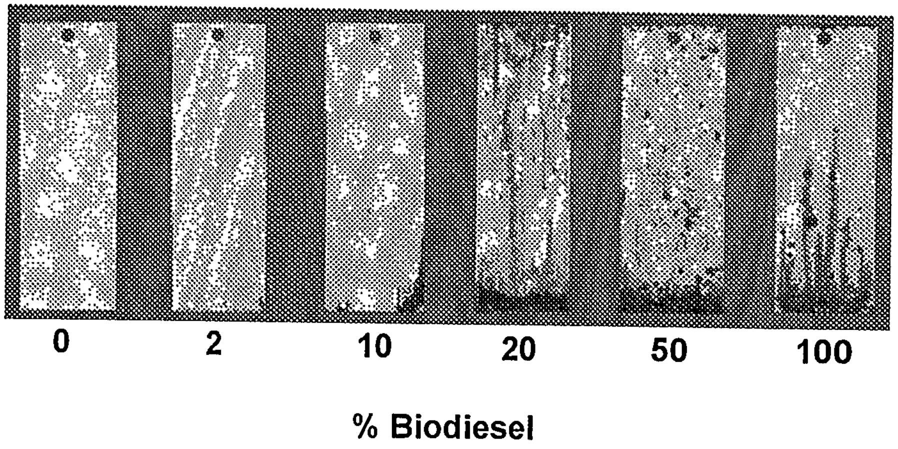


Figure 6

40 - Hour Stability with Steel Strip
Effect of Additives on 50/50 FO2/Biodiesel Blend

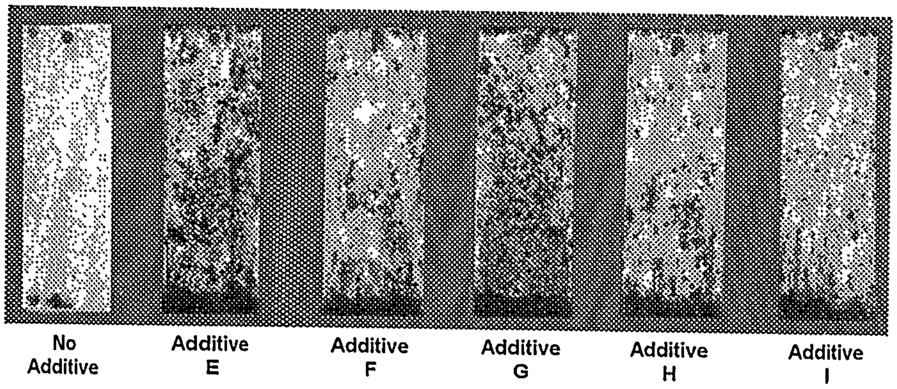


Figure 7

Cold Flow Properties of LS FO2/ Biodiesel Blends

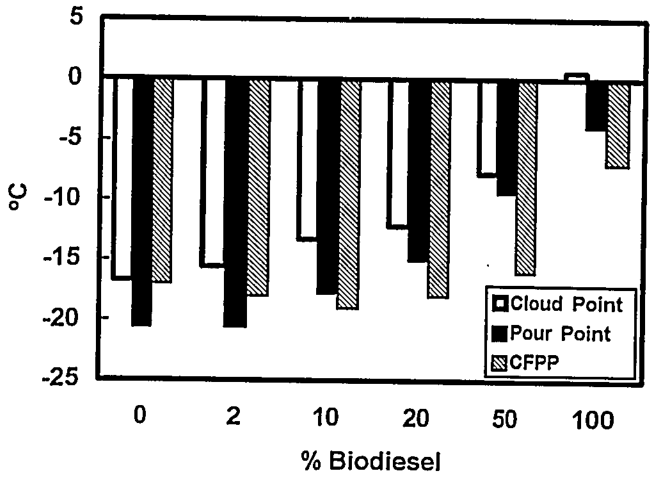
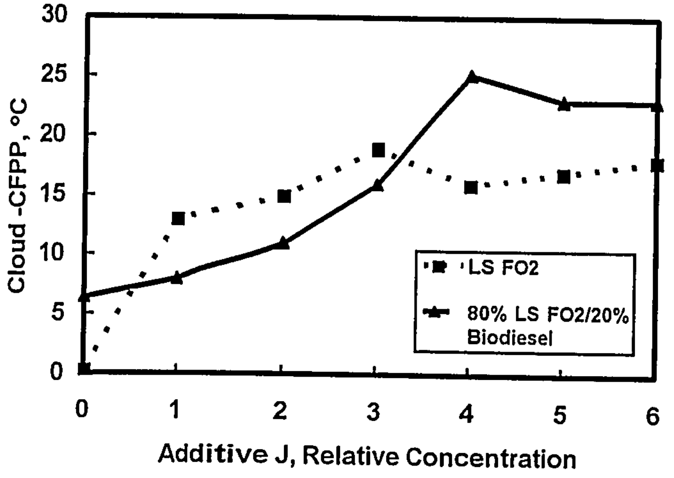


Figure 8

Effect of Cold Flow Additive on CFPP



IASH '97, the 6th International Conference on Stability and Handling of Liquid Fuels

Vancouver, B. C., Canada
October 12-17, 1997

OXIDATION STABILITY OF FATTY ACID METHYL ESTERS USED AS DIESEL FUEL SUBSTITUTE

P. Hödl*, M. T. Rodo-Cima, H. Schindlbauer, N. Simkovsky and W. Tuechler

Research Institute for Chemistry and Technology of Petroleum Products, Vienna University of Technology, Getreidemarkt 9 / 190, A-1060 Vienna, Austria

The oxidation stability of fatty acid methyl esters (FAME) used as diesel fuel substitute is an important feature, which describes the storage possibilities. Due to their very different chemical structure and resulting higher reactivity as compared to petroleum middle distillates FAME are more subjected to oxidation processes as well as autooxidation. The unsaturated components of the biogenic fuel are mainly responsible for this higher reactivity. The oxidation process leads to undesirable properties, like higher viscosity due to polymerisation or enhanced corrosive effects, caused by short chained free acids. Within this work a few general test methods for the determination of the oxidation stability should be highlighted as well as two very specific ones. These two methods, a modified IP- 306 method and the „Baader Test", of which the IP-306 should be included within the European Standard Specification for FAME used as Diesel Fuel Substitute, will be correlated and compared. The FAME used in these investigations were of different age and origin, and we will show, that, besides other properties of the oil, the production process of the FAME has an important influence on the oxidation stability.

6th International Conference
on Stability and Handling
of Liquid Fuels

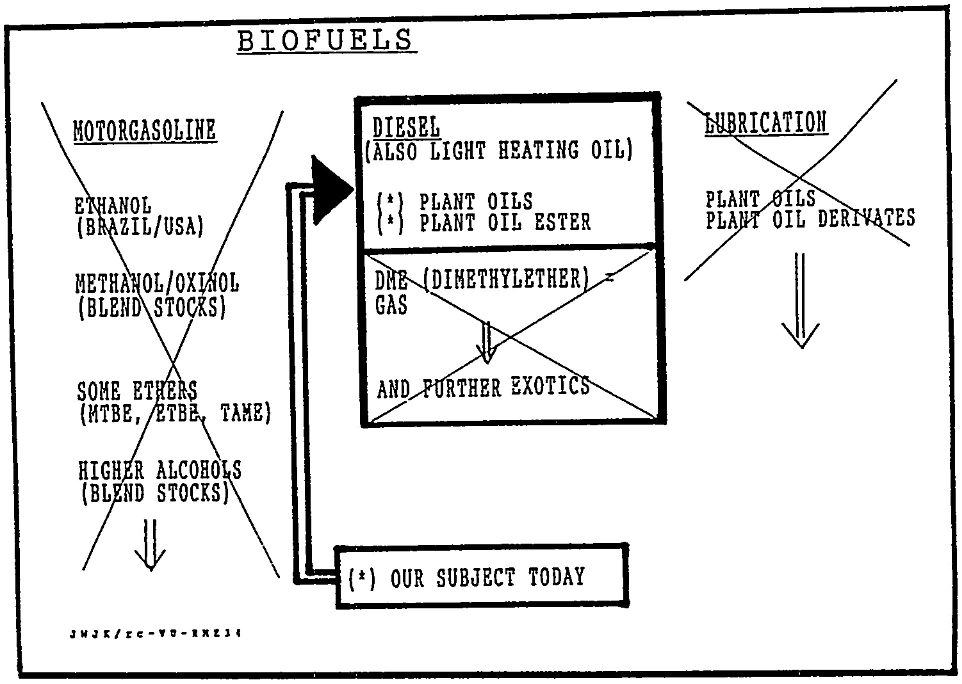
Vancouver, Canada October 13-17, 1997

Biodiesel, an Environmental Blessing or a Biodegradation Headache for Long Term Storage

J.W. Joachim Koenig
ERDÖLBEVORRATUNGSVERBAND
(German Strategic Petroleum Reserve)
Jungfernstieg 38
20345 Hamburg, Germany

Chairman, Ladies and Gentlemen,

Biofuels are being used for motor vehicles since many years. Mr. Diesel, when demonstrating one of his first engines used plant oil, crude oil derived diesel fuel not having been developed then. But with the rapid development of motorization and low cost mineral oils becoming available in the US and Europe people forgot agriculture as fuel source, even though experimentation never ceased totally. Even when mineral oil became scarce during WWII the general food shortage prevented the use of vegetable/animal oil or greases as fuel for cars. In Germany towards the end of the war biomass (wet wood cuttings) were used to produce "water gas" in reactors carried along by cars. Only after the first world oil crisis in 1974 when crude prices increased tenfold from 1.80 - 2.00 US$/bbl people started to remember that agriculture surplus capacity could potentially be used to produce fuels. As both the US and European community had large surplus land and farmers needed government support, sizeable biofuel programmes were started. More or less in parallel large sugar cane surplus and shortage of hard currency drove Brazil into an ethanol production programme. Since the US fuel market is and always was dominated by Otto engines using gasolines, the US biofuel programmes were mainly alcohol based. In contrast in Europe with its long tradition of diesel engined passenger cars the farming industry was experimenting with plant oils of almost every oil containing plant growing in a European climate. Both the pure oils as well as chemical derivates were tested and originally both found their niche applications e.g. in lubrication, cutting oils, hydrolics etc.



BIOFUELS

MOTORGASOLINE

ETHANOL
(BRAZIL/USA)

METHANOL/OXINOL
(BLEND STOCKS)

SOME ETHERS
(MTBE, ETBE, TAME)

HIGHER ALCOHOLS
(BLEND STOCKS)

DIESEL
(ALSO LIGHT HEATING OIL)

(*) PLANT OILS
(*) PLANT OIL ESTER

DME (DIMETHYLETHER)
GAS

AND FURTHER EXOTICS

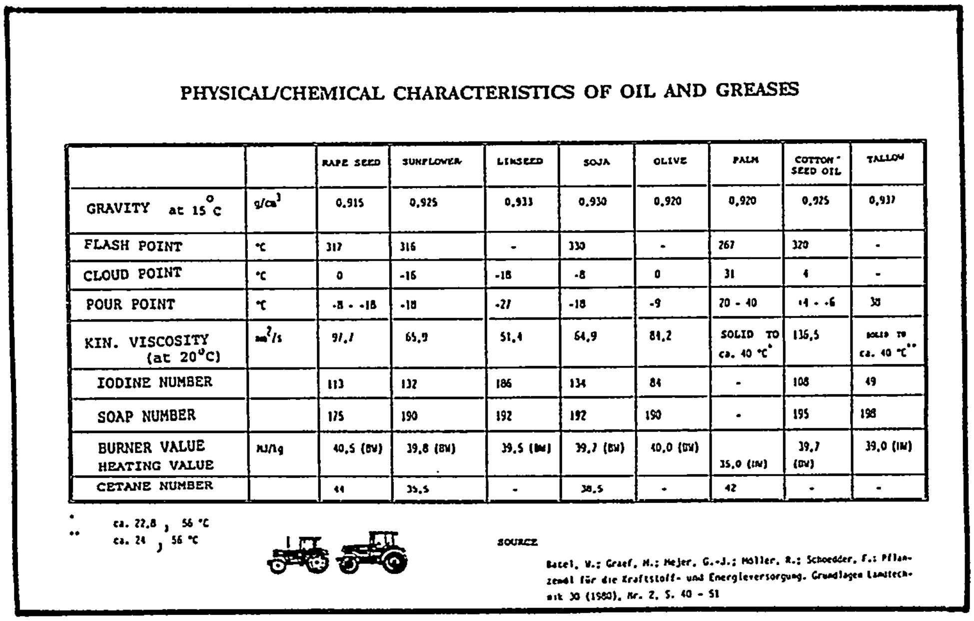
LUBRICATION

PLANT OILS
PLANT OIL DERIVATES

(*) OUR SUBJECT TODAY

JWJK/ec-VO-EKE34

Todays paper will cover the biodiesel story only, leaving all other biofuels aside.



PHYSICAL/CHEMICAL CHARACTERISTICS OF OIL AND GREASES

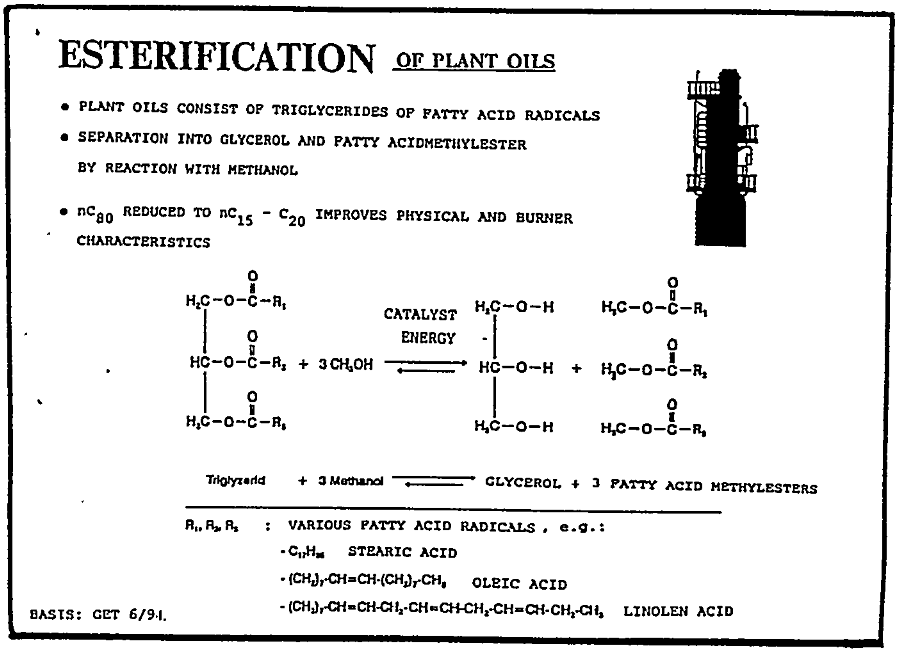
		RAPE SEED	SUNFLOWER	LINSEED	SOJA	OLIVE	PALM	COTTON-SEED OIL	TALLOW
GRAVITY at 15 °C	g/cm³	0,915	0,925	0,933	0,930	0,920	0,920	0,925	0,937
FLASH POINT	°C	317	316	-	330	-	267	320	-
CLOUD POINT	°C	0	-16	-18	-8	0	31	4	-
POUR POINT	°C	-8 - -18	-18	-27	-18	-9	20 - 40	+4 - -6	30
KIN. VISCOSITY (at 20°C)	mm²/s	97,7	65,9	51,4	64,9	84,2	SOLID TO ca. 40 °C*	136,5	SOLID TO ca. 40 °C**
IODINE NUMBER		113	132	186	134	84	-	108	49
SOAP NUMBER		175	190	192	192	190	-	195	198
BURNER VALUE HEATING VALUE	MJ/kg	40,5 (BV)	39,8 (BV)	39,5 (BV)	39,7 (BV)	40,0 (BV)	35,0 (HV)	39,7 (BV)	39,0 (HV)
CETANE NUMBER		44	35,5	-	38,5	-	42	-	-

* ca. 22,8 , 56 °C
** ca. 24 , 56 °C

SOURCE

Batel, W.; Graef, M.; Mejer, G.-J.; Möller, R.; Schoedder, F.: Pflanzenöl für die Kraftstoff- und Energieversorgung. Grundlagen Landtechnik 30 (1980), Nr. 2, S. 40 - 51

Biodiesel can be produced from any oils (plant or animal) fitting into the gravity and right boiling range and normally not exceeding a carbon number of ca. 80, even though there are large differences as can be seen on this view graph. Please note the large differences in cold properties and viscosities. As a result the pure oils are useable only in summer (unless preheated in the tank) and not very practical for passenger cars. Tractors in Austria though use it in farming due to the low cost.



ESTERIFICATION OF PLANT OILS

- PLANT OILS CONSIST OF TRIGLYCERIDES OF FATTY ACID RADICALS
- SEPARATION INTO GLYCEROL AND FATTY ACIDMETHYLESTER BY REACTION WITH METHANOL
- nC_{80} REDUCED TO $nC_{15}-C_{20}$ IMPROVES PHYSICAL AND BURNER CHARACTERISTICS

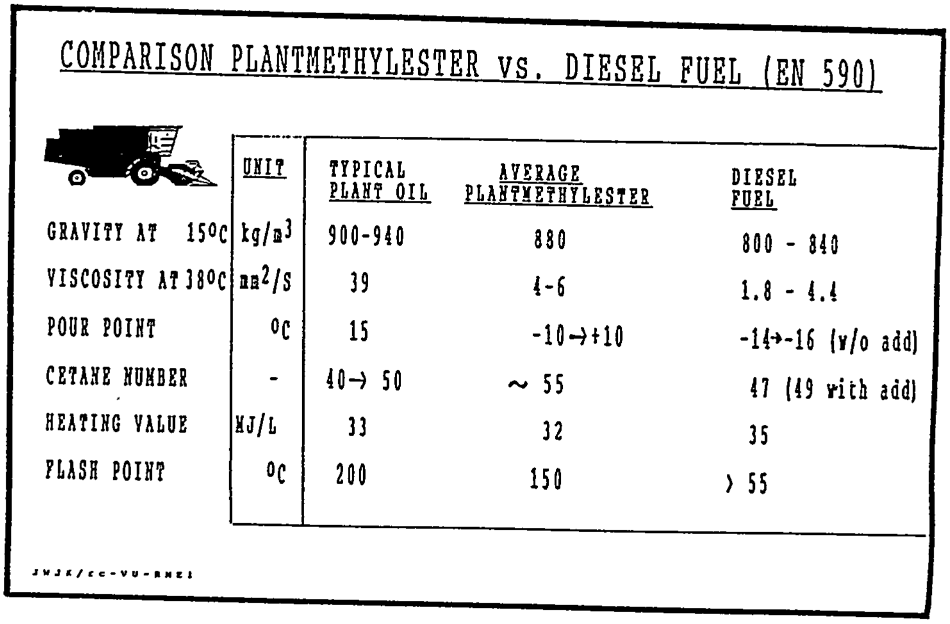
$$\begin{array}{lcccccc}
H_2C-O-\overset{O}{\overset{\|}{C}}-R_1 & & & & H_2C-O-H & & H_3C-O-\overset{O}{\overset{\|}{C}}-R_1\\
| & & & \text{CATALYST ENERGY} & | & & \\
HC-O-\overset{O}{\overset{\|}{C}}-R_2 & + & 3CH_3OH & \rightleftharpoons & HC-O-H & + & H_3C-O-\overset{O}{\overset{\|}{C}}-R_2\\
| & & & & | & & \\
H_2C-O-\overset{O}{\overset{\|}{C}}-R_3 & & & & H_2C-O-H & & H_3C-O-\overset{O}{\overset{\|}{C}}-R_3
\end{array}$$

Triglyzerid + 3 Methanol $\rightleftharpoons$ GLYCEROL + 3 FATTY ACID METHYLESTERS

R_1, R_2, R_3 : VARIOUS FATTY ACID RADICALS , e.g.:
- $C_{17}H_{35}$ STEARIC ACID
- $(CH_2)_7-CH=CH-(CH_2)_7-CH_3$ OLEIC ACID
- $(CH_2)_7-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$ LINOLEN ACID

BASIS: GET 6/91.

A way to solve the viscosity and often severe cold property problems is the esterification of the oil or grease triglycerides by reaction over methanol and catalyst, which results in glycerol and three fatty acid methyl esters, thus reducing the molecule size to around 15 to 20 carbon atoms. One should note here that the concept of biological production is violated by using methanol, which normally is produced in Europe from natural gas and not from fermentation of biomass.

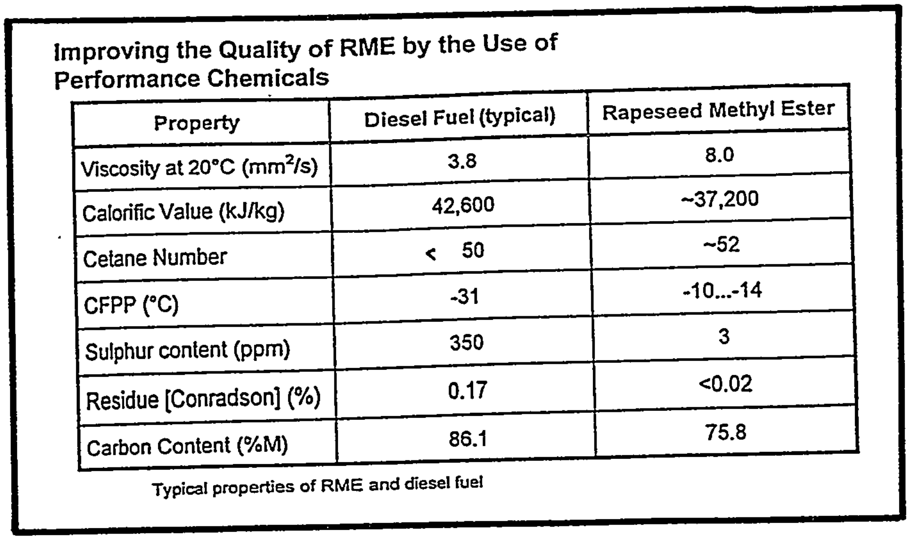


COMPARISON PLANTMETHYLESTER vs. DIESEL FUEL (EN 590)

	UNIT	TYPICAL PLANT OIL	AVERAGE PLANTMETHYLESTER	DIESEL FUEL
GRAVITY AT 15°C	kg/m³	900-940	880	800 - 840
VISCOSITY AT 38°C	mm²/S	39	4-6	1.8 - 4.4
POUR POINT	°C	15	-10→+10	-14→-16 (w/o add)
CETANE NUMBER	-	40→ 50	~ 55	47 (49 with add)
HEATING VALUE	MJ/L	33	32	35
FLASH POINT	°C	200	150	> 55

JWJK/cc-VU-RNE1

The esterification brings the fuel into property ranges rather similar to mineral oil based diesel fuel. Plant methyl esters normally have excellent cetane numbers, but depending on the composition of the fatty acids composing the plant oil the resulting esters still can have cold property problems. Heating values are of course lower due to the oxygen content of esters. High flash points are generally but not always an advantage.



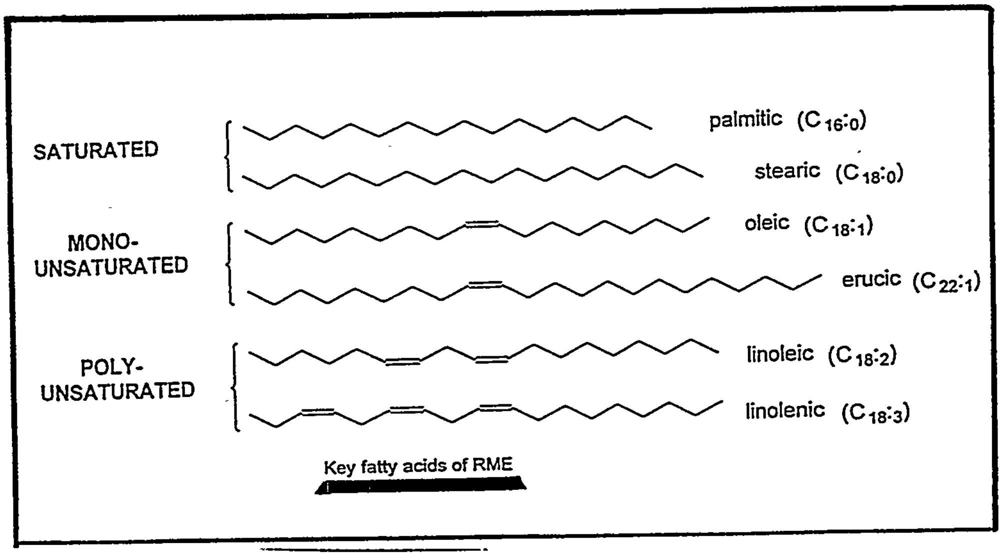
Improving the Quality of RME by the Use of Performance Chemicals

Property	Diesel Fuel (typical)	Rapeseed Methyl Ester
Viscosity at 20°C (mm^2/s)	3.8	8.0
Calorific Value (kJ/kg)	42,600	~37,200
Cetane Number	< 50	~52
CFPP (°C)	-31	-10...-14
Sulphur content (ppm)	350	3
Residue [Conradson] (%)	0.17	<0.02
Carbon Content (%M)	86.1	75.8

Typical properties of RME and diesel fuel

D.WILSON
Lubrizol International Laboratories, Derby, United Kingdom

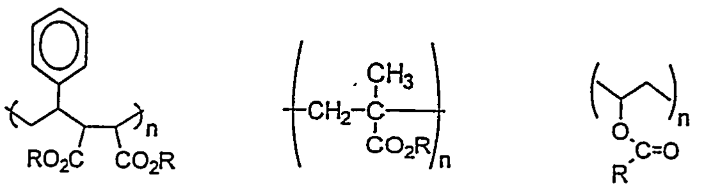
Of all the possible options, in Europe rape seed oil methyl ester was found to be closest to mineral oil based diesels. Please note the low sulfur content. While the rape plant contains a fair amount of sulfur (hence its yellow blooms in polluted areas near highways), the RME is almost sulfur free. Also ConCarbon, a measure for particulate formation is extremely advantageous for the environment.



Key fatty acids of RME

There are many different types of rape seed oils depending on the relative content of saturated and unsaturated fatty acids. Farming can selectively improve and optimize the composition, so that modern "breeds" come very close to performance characteristics of mineral oil diesels. This vu-graph shows the main components, other fatty acids in small percentages may also occur. What remains as a big handling problem is the still poor cold property of RME.

Improving the Quality of RME by the Use of Performance Chemicals



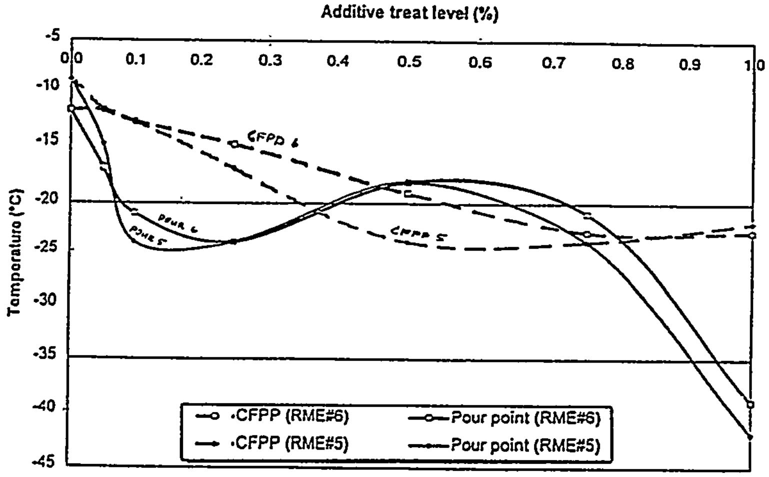
MALAN-STYRENE ESTER POLYMETHACRYLATE ETHYLENE VINYL ACETATE

Pour point depressant chemistry.

D.WILSON
Lubrizol International Laboratories, Derby, United Kingdom

One tries to conquer the problem by additivation. There are many different pour point and CFPP (cold filter plugging point) additives in the market of which three are shown here.

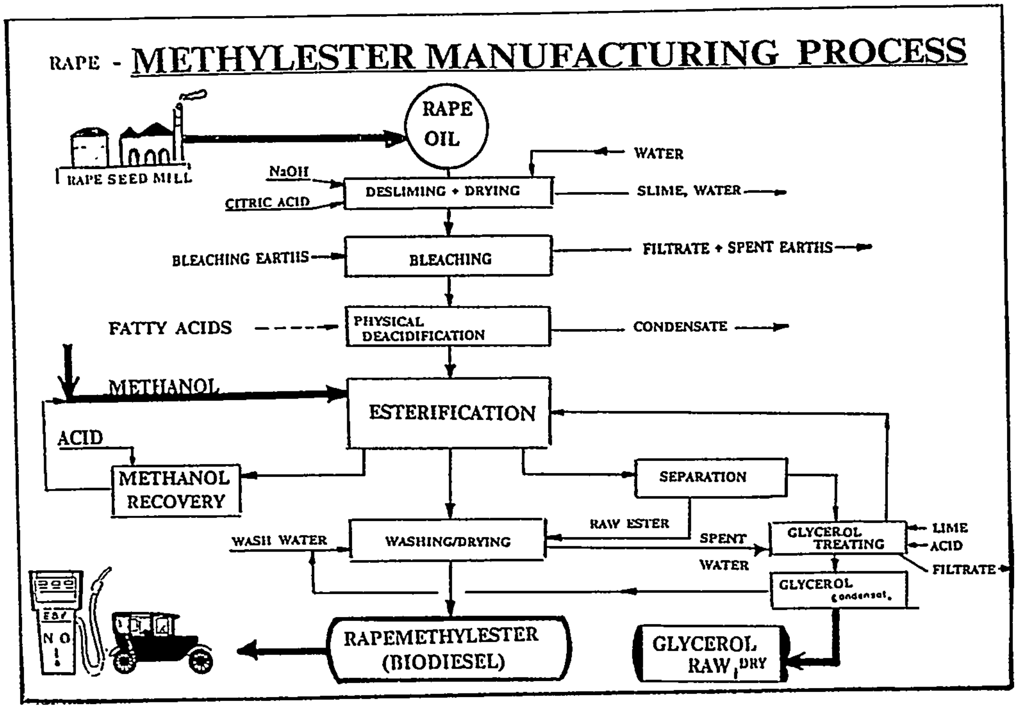
Improving the Quality of RME by the Use of Performance Chemicals



Low temperature performance of PPD#1 in RME's #5 & #6

D.WILSON
Lubrizol International Laboratories, Derby, United Kingdom

One gets however rather strange results quite untypical from cold property improvers in mineral oil based diesel fuels. I have borrowed a chart from Lubrizol shown earlier this year at the Stuttgart International Fuels symposium. At low treat levels additives showed good effectiveness with pour point and CFPP getting worse when level is increased and pour exceeding CFPP, no doubt a test method anomaly. The explanation given was the additive effectiveness of keeping crystals small and apart from agglomerations, the CFPP test reacting only to the crystal sizes.


RAPE - METHYLESTER MANUFACTURING PROCESS

Before continuing with the environmental issue allow me to briefly show you a flow plan of the manufacturing process. Harvested rape seeds will be milled to rape seed oil, which after desliming, drying and bleaching and physical deacidification produces fatty acids, byproducts being slimes, filtrates, acid condensates. In a reactor over catalyst methanol is added forcing the esterification to glycerol and methylester. Surplus methanol is recovered and recycled, glycerol separated from RME, glycerol treated and dried to produce a saleable raw glycerol, RME being washed and dried to become a finished biodiesel. As I said before, the methanol is not normally of bio-origin as a renewable resource. As the whole process of an RME-refinery is acidic at various process stages the use of non-corrosive alloy steel is compulsory.

BIODIESEL - "a HOT DEBATE"

CLAIMS	STATUS OF DISCUSSION
PRO	
• positive energy balance	disputed
• independance of imports	limited value
• closed CO_2 circuit	accepted
• free of sulfur, low in emissions/particulates	partly true
• easy degradation	accepted, potentially problem
• economical and environmentally sound use of farming	strongly disputed
CONTRA	
• monoculture	results not yet understood
• very limited capacity	accepted
• high cost/requires tax support	understood
• less energy content, engine problems	solved by industry
• emotionally political	continues since years
• winter problems	can be corrected
• less CO_2 but more CH_4, NO_x, laughing gas (N_2O)	emissions accepted
• easiliy degradable/storage problems	our issue today

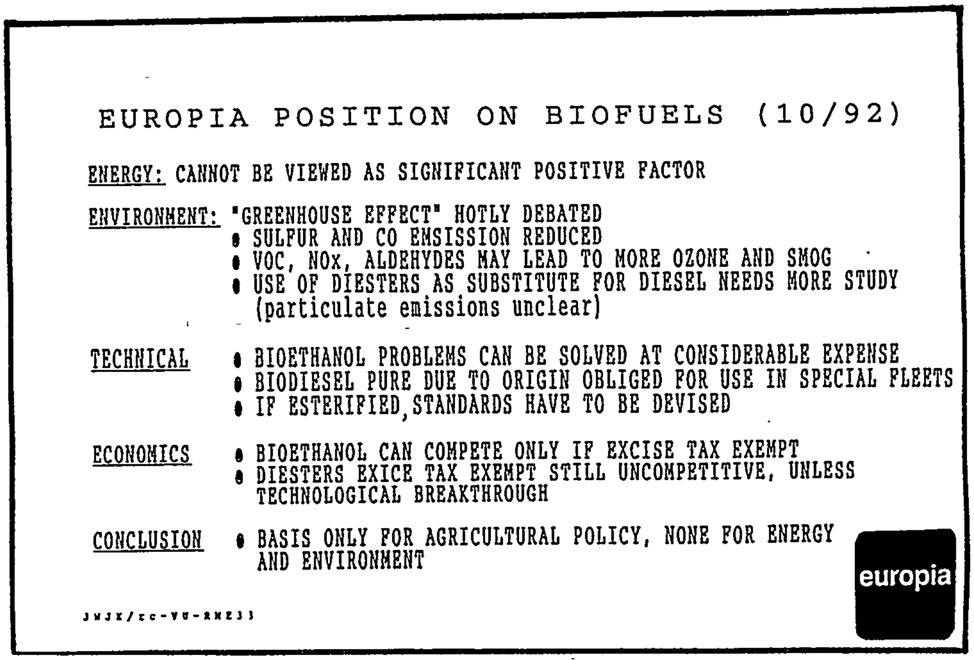
JWJK/CC-VU-RMZ4

Economics and environmental and engine performance benefits are hotly debated issues. I have listed here the main points. Both "pros" and "cons" depend highly on the point of view. The energy balance (consumes more energy than it provides) depends highly on the circle one draws around the generation of RME. If all tool making, agricultural consumption (energy, fertilizers etc.) and lower mileage are included, the modern production lines may gradually reach balance, in the earlier days of small scale operation and poor logistics it was clearly negative. Generally accepted are the closed CO_2 circuit, low sulfur and particulates emissions and easier degradation. However one should not discard problems of more methane, NO_x, laughing gas (N_2O) emissions too easily. Environmentally sound farming, huge tax support requirement, monoculture and shrinking farm land capacity are strongly emotional issues in Europe, though there are also strong differences between European countries.

BIODIESEL IN USE IN EUROPE

France:	BLENDED INTO NORMAL DIESEL AT 5% TO SUPPORT FARMERS. ELF/TOTAL MAINLY INVOLVED. PLANS TO MAKE IT COMPULSORY NOW ALSO USE IN HOME HEATING OIL
Italy:	AVAILABLE AS RME PURE AND BLEND STOCK, PUSHED BY MANUFACTURING AGRICULTURAL LOBBY.
Austria:	WIDESPREAD IN USE AS RAPE SEED OIL AND RME. LONG EXPERIENCE
Sweden:	WIDE USE, MAINLY AS CLEAN FUEL "CITY DIESEL". EXPENSIVE BUT WITH SOME EXCEPTIONAL QUALITIES.
Germany:	LOCAL CENTRES OF USE IN CITIES, OFTEN PUSHED BY LOCAL GOVERNMENTS; MAINLY AS RME PURE, NO USE OF RAPE SEED OIL. > 250 GAS STATIONS. PRELIMINARY SPECIFICATION ISSUED BY DIN. GERMAN GOVERNMENT DIVIDED.
E.U.:	UNDER STRONG FRENCH/ITALIEN/SWEDISH SUPPORT.COMPULSORY BLENDING REGULATION FAILED. STRONG INTEREST OF PUBLIC AND GOVERNMENTS THROUGHOUT. NO TAX HARMONIZATION YET.

The main push for RME use comes from the French and Italian farming lobby, who act quite successfully at the EU in Brussels. At the request of the European Commission both RME as well as RME blends with mineral oil sourced diesel are being normed by CEN at the moment. Final and/or preliminary norms exist in several countries since some years. While Germany sees a market for pure RME as biodiesel only (tax driven) in France RME is used as by-blend up to 5% and 10% are being discussed, 5% possibly becoming compulsory. The French domestic heating oil sector sees strong benefits from RME as oxygenates to improve burning characteristics, as the high diesel share of the middle distillate pool forces poorly burning heavy crack aromatics into heating oil due to tight diesel European specifications. Governments and the mineral oil industry remain deeply divided on the value of this alternative fuel, even the German environmentalists have serious concern for fear of large monocultures.



EUROPIA POSITION ON BIOFUELS (10/92)

ENERGY: CANNOT BE VIEWED AS SIGNIFICANT POSITIVE FACTOR

ENVIRONMENT: "GREENHOUSE EFFECT" HOTLY DEBATED
- SULFUR AND CO EMSISSION REDUCED
- VOC, NOx, ALDEHYDES MAY LEAD TO MORE OZONE AND SMOG
- USE OF DIESTERS AS SUBSTITUTE FOR DIESEL NEEDS MORE STUDY (particulate emissions unclear)

TECHNICAL
- BIOETHANOL PROBLEMS CAN BE SOLVED AT CONSIDERABLE EXPENSE
- BIODIESEL PURE DUE TO ORIGIN OBLIGED FOR USE IN SPECIAL FLEETS
- IF ESTERIFIED, STANDARDS HAVE TO BE DEVISED

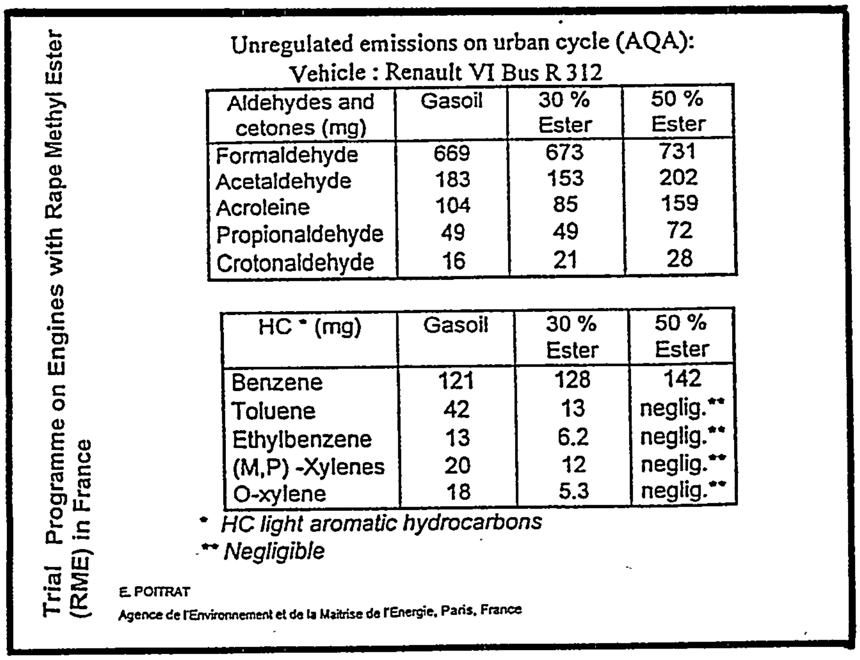
ECONOMICS
- BIOETHANOL CAN COMPETE ONLY IF EXCISE TAX EXEMPT
- DIESTERS EXICE TAX EXEMPT STILL UNCOMPETITIVE, UNLESS TECHNOLOGICAL BREAKTHROUGH

CONCLUSION
- BASIS ONLY FOR AGRICULTURAL POLICY, NONE FOR ENERGY AND ENVIRONMENT

JWJX/cc-VU-RME33

europia

The European oil industry issued in 1992 a balanced view on RME concluding that it may be a basis for agricultural policy but does little to nothing for energy security and the environment.



Trial Programme on Engines with Rape Methyl Ester (RME) in France

Unregulated emissions on urban cycle (AQA):
Vehicle : Renault VI Bus R 312

Aldehydes and cetones (mg)	Gasoil	30 % Ester	50 % Ester
Formaldehyde	669	673	731
Acetaldehyde	183	153	202
Acroleine	104	85	159
Propionaldehyde	49	49	72
Crotonaldehyde	16	21	28

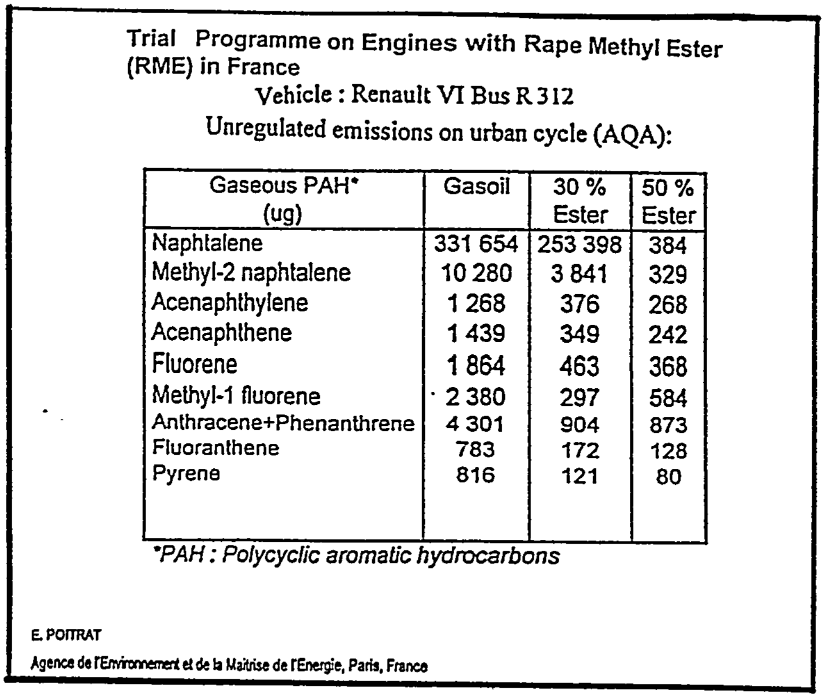
HC * (mg)	Gasoil	30 % Ester	50 % Ester
Benzene	121	128	142
Toluene	42	13	neglig.**
Ethylbenzene	13	6.2	neglig.**
(M,P) -Xylenes	20	12	neglig.**
O-xylene	18	5.3	neglig.**

* *HC light aromatic hydrocarbons*

** *Negligible*

E. POITRAT
Agence de l'Environnement et de la Maitrise de l'Energie, Paris, France

Allow me here to go back briefly to emissions which we touched upon earlier. A very interesting study by the Agence de l'Environment et de la Maitrise de l'Energy (Paris) France was presented by Mr. Poitrat at the 1st International Fuels Symposium in Stuttgart in January this year. It compared ordinary diesel with blends of 30% or 50% RME with ordinary diesel for Renault city buses.
It clearly showed a sizeable increase of aldehyde emissions, also benzene emissions increased with RME additions while heavier aromatics are obviously suppressed.



Trial Programme on Engines with Rape Methyl Ester (RME) in France

Vehicle : Renault VI Bus R 312

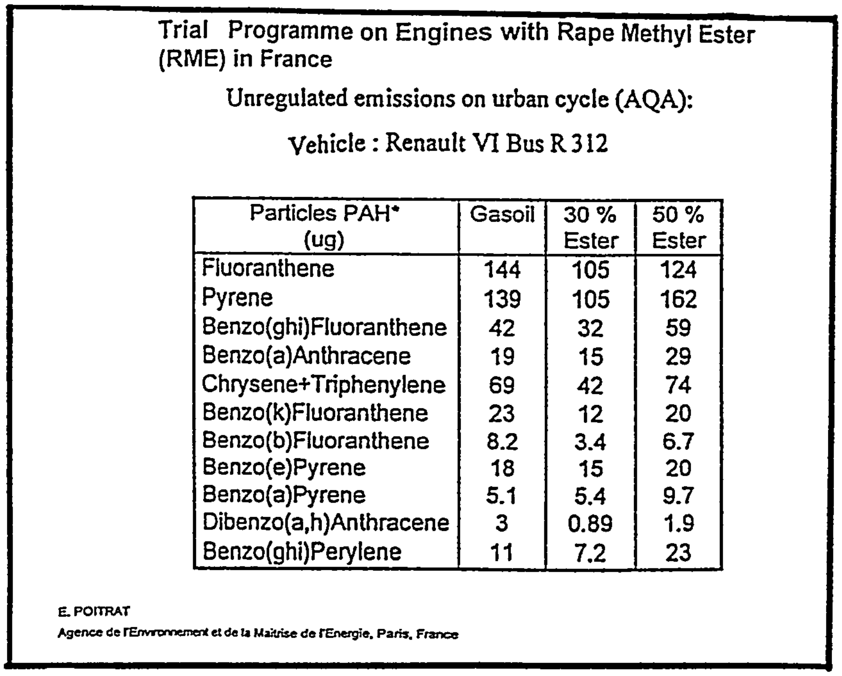
Unregulated emissions on urban cycle (AQA):

Gaseous PAH* (ug)	Gasoil	30 % Ester	50 % Ester
Naphtalene	331 654	253 398	384
Methyl-2 naphtalene	10 280	3 841	329
Acenaphthylene	1 268	376	268
Acenaphthene	1 439	349	242
Fluorene	1 864	463	368
Methyl-1 fluorene	2 380	297	584
Anthracene+Phenanthrene	4 301	904	873
Fluoranthene	783	172	128
Pyrene	816	121	80

**PAH : Polycyclic aromatic hydrocarbons*

E. POITRAT

Agence de l'Environnement et de la Maitrise de l'Energie, Paris, France



Trial Programme on Engines with Rape Methyl Ester (RME) in France

Unregulated emissions on urban cycle (AQA):

Vehicle : Renault VI Bus R 312

Particles PAH* (ug)	Gasoil	30 % Ester	50 % Ester
Fluoranthene	144	105	124
Pyrene	139	105	162
Benzo(ghi)Fluoranthene	42	32	59
Benzo(a)Anthracene	19	15	29
Chrysene+Triphenylene	69	42	74
Benzo(k)Fluoranthene	23	12	20
Benzo(b)Fluoranthene	8.2	3.4	6.7
Benzo(e)Pyrene	18	15	20
Benzo(a)Pyrene	5.1	5.4	9.7
Dibenzo(a,h)Anthracene	3	0.89	1.9
Benzo(ghi)Perylene	11	7.2	23

E. POITRAT

Agence de l'Environnement et de la Maitrise de l'Energie, Paris, France

Looking at polycyclic aromatic hydrocarbons - potentially and known carcenogenies - a very drastic decrease was found with RME addition, an even better result could of course be achieved with pure RME. Unfortunately this is not the case with all PAH, some rather worrysome ones like benzopyrenes unfortunately show increases, though not as drastic as the decreases shown on the previous chart.

BIO-GREEN-ECOLOGICAL FUELS

BIODEGRADATION

AFTER USE

PLEASE NOT BEFORE OR

IN USE !

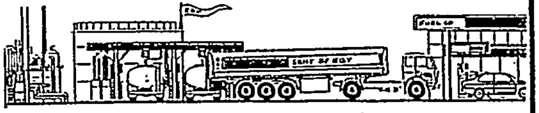
JWJK/EC-VU-RME15

Let us now come to one of the big issues in quality deterioration and handling of RME and or RME blends. The rapid degradation characteristics in the environment are well known and treasured by historic users of RME, like in chain saw lubrication, hydrolic machinery, outboard boot engines etc. However our fuel should please not deteriorate already in storage tanks, filling stations, transport vessels and customer tanks. The objective must be to create an RME fuel which should not start biodeterioration earlier than mineral oil based diesel and which produces comparable amounts of biomass over identical storage times.

EBV-CONCERNS ABOUT RME-BIOFUELS

STORAGE BY EBV AS RME (pure) UNLIKELY SINCE FARMER'S SUPPLY POTENTIAL TOO SMALL

- would be problematic due to water take-up in long term storage



MORE LIKELY

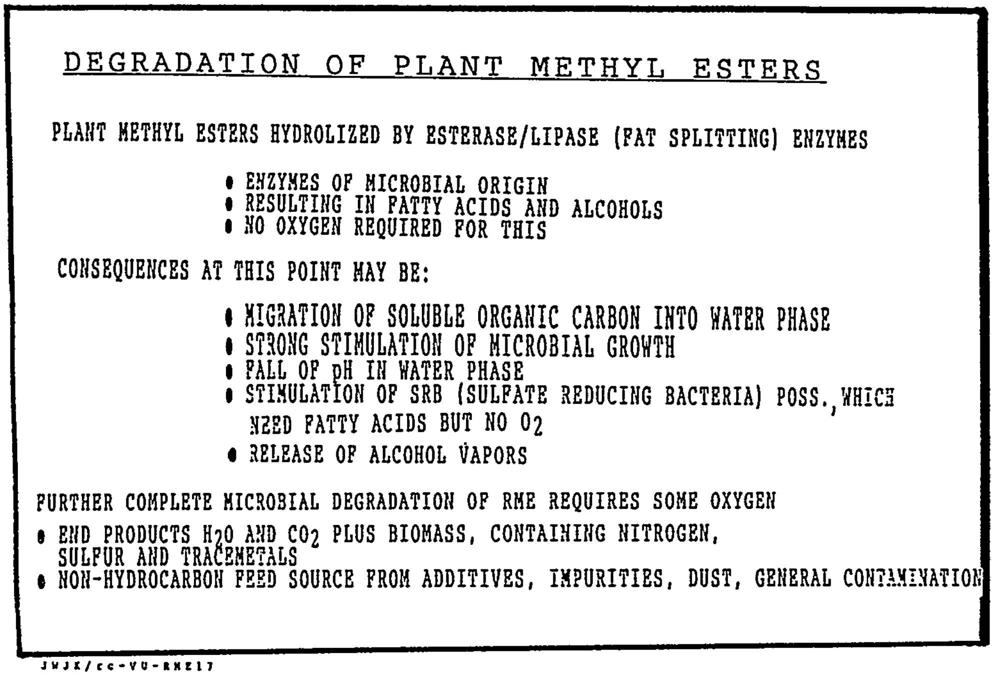
- conventional diesel with 1, 5, 10% RME as blend stocks to support farmers
- manufacturing and logistics systems contaminated by RME at very small level, since separate RME systems to costly with small volume throughput of pure RME fuels
- cross border contamination, even if not blended in Germany !; retail customers (mainly home heating oil) and bulk users of diesel may suffer

CONCLUSION: the "more likely" cases are more or less here today

QUESTION: how much more vulnerable against microbial growth are RME blends with diesel or RME-contaminated heating oils/diesel fuels compared to pure diesel and/or pure RME ?

Middle distillate systems are very difficult to be kept water free and unfortunately RME is highly hygroscopic. While ordinary diesel in long term storage will dissolve hardly ever more than 100 ppm water, RME can dissolve easily 1000-2000 ppm if exposed to water over a longer period - a perfect base for microbial growth.

EBV the German Strategic Petroleum reserve will for these reasons not buy RME or RME blends. But as the logistics system due to the parallel use of RME and ordinary diesel in Germany gradually gets contaminated with traces or small percentages of RME - which also may come through cross broder traffic - EBV wanted to know how such spoiling of the system could influence longevity of diesel stocks.



DEGRADATION OF PLANT METHYL ESTERS

PLANT METHYL ESTERS HYDROLIZED BY ESTERASE/LIPASE (FAT SPLITTING) ENZYMES

- ENZYMES OF MICROBIAL ORIGIN
- RESULTING IN FATTY ACIDS AND ALCOHOLS
- NO OXYGEN REQUIRED FOR THIS

CONSEQUENCES AT THIS POINT MAY BE:

- MIGRATION OF SOLUBLE ORGANIC CARBON INTO WATER PHASE
- STRONG STIMULATION OF MICROBIAL GROWTH
- FALL OF pH IN WATER PHASE
- STIMULATION OF SRB (SULFATE REDUCING BACTERIA) POSS., WHICH NEED FATTY ACIDS BUT NO O_2
- RELEASE OF ALCOHOL VAPORS

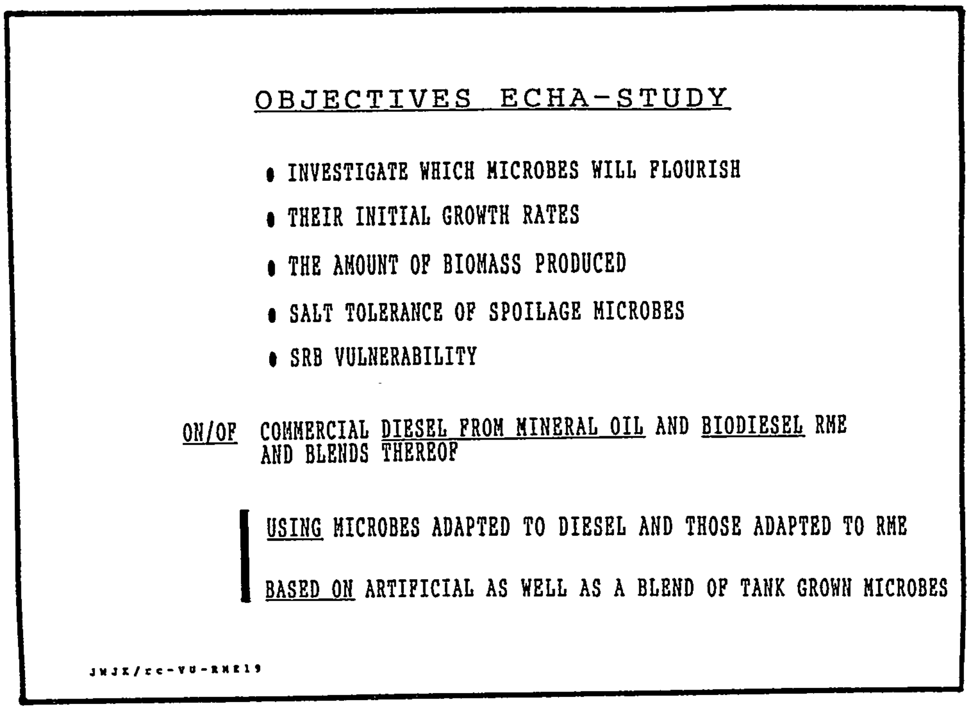
FURTHER COMPLETE MICROBIAL DEGRADATION OF RME REQUIRES SOME OXYGEN

- END PRODUCTS H_2O AND CO_2 PLUS BIOMASS, CONTAINING NITROGEN, SULFUR AND TRACEMETALS
- NON-HYDROCARBON FEED SOURCE FROM ADDITIVES, IMPURITIES, DUST, GENERAL CONTAMINATION

JWJK/cc-VU-RME17

The degradation process of plant methyl esters can be characterized by fat splitting enzymes which hydrolize PME (esterase/lipase). The enzymes originate from microbes, resulting in fatty acids and alcohols, no oxygen is needed for this, in a way partly a reversal of the RME production process. At this phase soluble organic carbon will enter the water phase and stimulates the microbial growth possibly resulting in a fall of the PH-value. Stimulation of sulfate reducers at tank bottoms using fatty acids but no oxygen and possibly release of alcohols vapors are dangers to watch. Further full degradation will be aerobic though, finally yielding water, carbon dioxyde and biomass, which will contain nitrogen, sulfur and trace metals. Microb cell requirements other than hydrocarbons are satisfied by e.g. additives, impurities, dust, rust and general sludge accumulated in tanks.

EBV ordered a research programme at ECHA Microbiology of Cardiff, UK to investigate the potential danger RME could pose to long term storage of commercial diesel with small RME contents.



OBJECTIVES ECHA-STUDY

- INVESTIGATE WHICH MICROBES WILL FLOURISH
- THEIR INITIAL GROWTH RATES
- THE AMOUNT OF BIOMASS PRODUCED
- SALT TOLERANCE OF SPOILAGE MICROBES
- SRB VULNERABILITY

ON/OF COMMERCIAL DIESEL FROM MINERAL OIL AND BIODIESEL RME
AND BLENDS THEREOF

USING MICROBES ADAPTED TO DIESEL AND THOSE ADAPTED TO RME

BASED ON ARTIFICIAL AS WELL AS A BLEND OF TANK GROWN MICROBES

JWJK/cc-VU-RME19

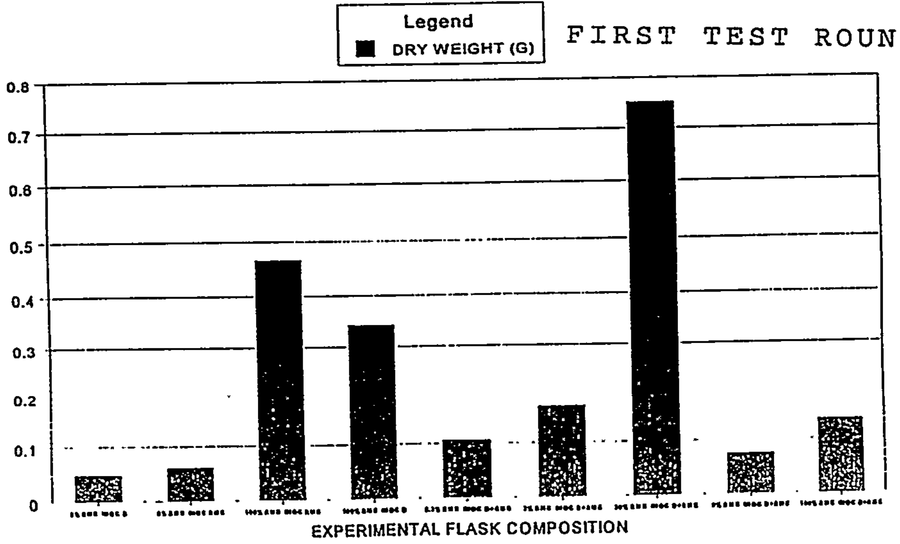
The detailed objectives are outlined in this vu-graph. Inocula were taken from UK-diesel, stale milk, Cardiff soil, cheese, Cardiff esturay mud, Russian gasoil, contaminated Hamburg harbour tanks. RME was from a German RME refinery. The UK sourced inocula were artificially adapted to diesel and RME, the German inocula were by definition adapted to diesel fuel since the microbes had been actively growing in Hamburg harbour tanks.

echa MICROBIOLOGY

BIOMASS EXPERIMENT

BIOMASS PRODUCTION AFTER 57 DAYS

FIRST TEST ROUND



One of the typical biomass results are shown here. The bars reach from 0% RME with a diesel adapted inoculum, over 0% RME with RME inoculum, over 100% RME with RME inoculum, over 100% RME with diesel inoculum, over 0,2%, 2%, 20% RME with the diesel and RME inoculum to 0% and 100% RME with the diesel and RME adapted inoculum. Please note the explosive biomass production at 20% RME with a combination inoculum which is 18 fold the biomass in a normal diesel with diesel adapted inoculum produces.

FINDINGS: BIOMASS

- RME PRODUCES MORE BIOMASS THAN DIESEL
- RME-OCULATED DIESEL PRODUCES MORE BIOMASS THAN DIESEL
- DIESEL-OCULATED RME PRODUCES 6.5 TIMES MORE BIOMASS THAN DIESEL OCULATED WITH DIESEL MICROBES

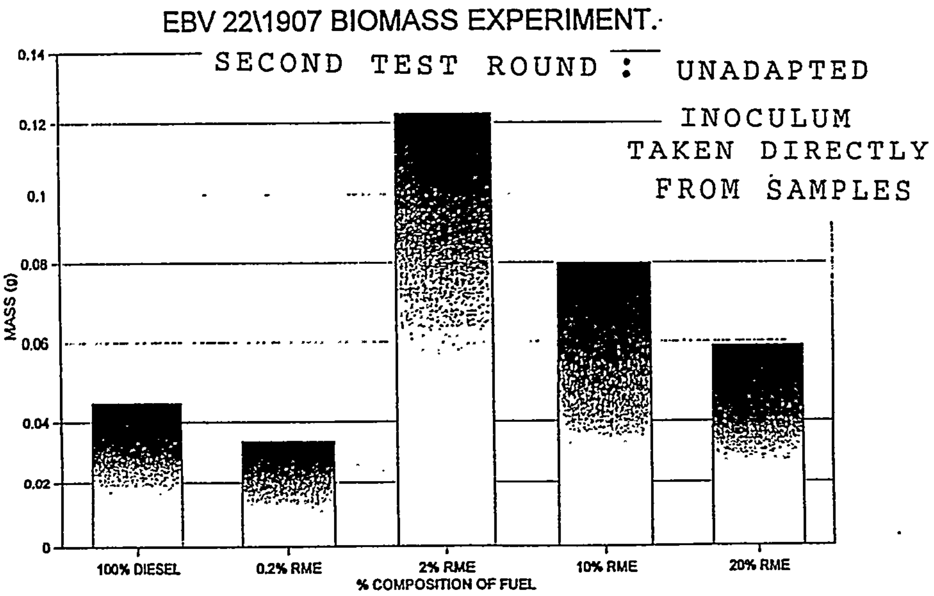
SUGGESTION: RME CAPABLE OF SUSTAINING GROWTH OF ORGANISMS THAT PRODUCE MORE BIOMASS

- AT LOW 0.2 % RME THE BIOMASS PRODUCTION IS ALREADY DOUBLED
- AT 20% RME IN FUEL AND RME-AND DIESEL-ADAPTED MICROBES PRESENT, BIOMASS PRODUCTION IS >15-FOLD COMPARED TO CONVENTIONAL DIESEL WITH DIESEL ADAPTED POPULATION

CAN THESE RESULTS BE REPEATED WITH DIFFERENT MICROB POPULATIONS? YES!

JWJE/cc-VU-ENE25

Here now we summarize our findings confirmed also by other test sets and by a parallel investigation at Oldenburg University of Germany.


EBV 22\1907 BIOMASS EXPERIMENT.

SECOND TEST ROUND : UNADAPTED INOCULUM TAKEN DIRECTLY FROM SAMPLES

Working with unadapted inocula produced naturally over the same time period lower overall biomass rates, but here the maximum appeared already at 2% RME in commercial diesel, the findings of this second test round are summarized as follows

FINDINGS: SECOND TEST ROUND (UNADAPTED MICROBES)

GROWTH RATE ANALYSIS

- A PERCENTAGE OF DIESEL TANK BACTERIAL FLORA ARE CAPABLE OF EVENTUALLY DEGRADING RME, WHETHER OR NOT RME IS PRESENT IN THE FUEL
- EXPOSURE OF FUEL BLEND OF 10% OR MORE RME FOR > 3 DAYS IS NECESSARY TO ACTIVATE RME DEGRADING METABOLIC PATHWAYS IMMEDIATELY
- EVEN THOUGH YEASTS WERE DETECTED IN THE INOCULA, THEY DID NOT SURVIVE, WHICH MEANS THEY ARE NOT READILY ADAPTABLE TO GROWTH ON RME, NO MOULD POPULATIONS WERE CAPABLE OF DEGRADING RME

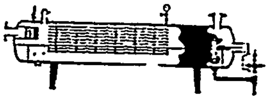
BIOMASS ANALYSIS

- UNADAPTED DIESEL MICROBES PRODUCE LESS BIOMASS THAN ADAPTED COLONIES OF THE FIRST TEST ROUND
- BIOMASS IN UNCONTAMINATED (100%) DIESEL IN BOTH ADAPTED AND UNADAPTED CASES ABOUT THE SAME, WHICH MEANS TANK FLORA PERFECTLY ADAPTED
- AVAILABILITY OF RME WILL EVENTUALLY PRODUCE DIESEL/RME ADAPTED FLORA THUS INCREASING BIOMASS SUBSTANTIALLY

JWJK/cc-VU-RME26

Further experiments covered the potential vulnerability to anaerob sulfate reducing bacteria (SRB) contamination. The conclusions are summarized in the following vu-graph.

CONCLUSIONS **SRB**

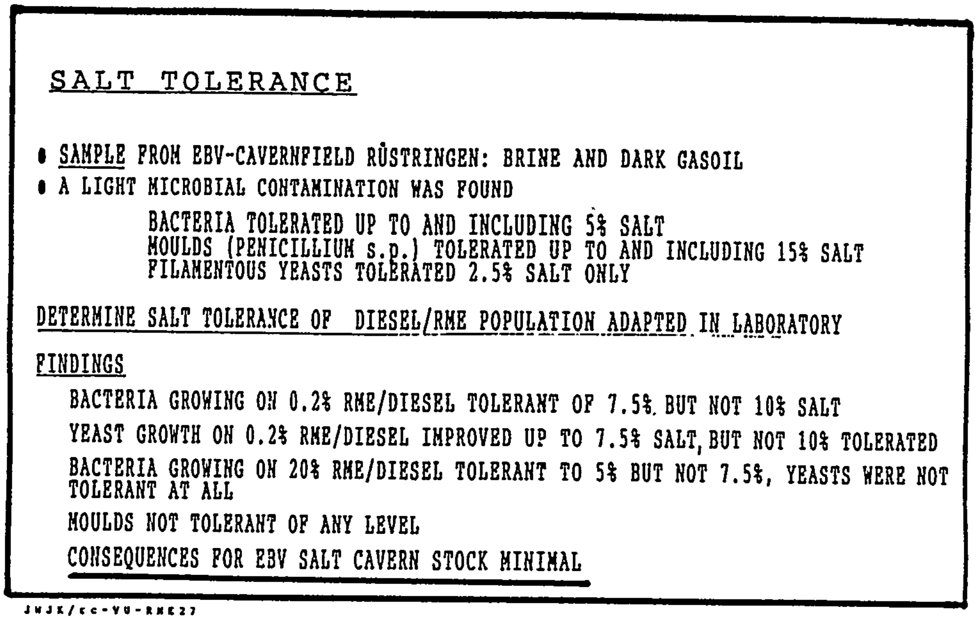


- FINAL ASSAY RESULTS SUGGEST SRB PROLIFERATION POSSIBLE IN RME FUELS
- TIME TO PRODUCE SRB IN HIGH NUMBERS LONGER THAN EXPECTED
- RESULTS INDICATE THAT SRB WILL PROLIFERATE EVENTUALLY, PROVIDED A SULFUR SOURCE IS AVAILABLE IN THE FUEL BLEND (FROM MINERAL OIL BASED DIESEL)OF > 10% RME OR GREATER
- EVEN THOUGH THERE WILL BE EVEN AT 0.05 wt% SULFUR DIESEL AND/OR AFTER CONTAMINATION WITH e.g. SEA WATER WITH ENOUGH SULFUR AND FREQUENTLY ALSO PHOSPHORUS AROUND,

▶ THE DANGER OF SRB DEVELOPMENT IN RME BLENDS IS POSSIBLY SMALLER THAN PREVIOUSLY FEARED ◀

In short words the danger of SRB development in RME blends is possibly smaller than previously feared.

Finally we needed to know whether RME contamination of cavern diesel was a real danger. The findings are highlighted below



SALT TOLERANCE

- SAMPLE FROM EBV-CAVERNFIELD RÜSTRINGEN: BRINE AND DARK GASOIL
- A LIGHT MICROBIAL CONTAMINATION WAS FOUND

BACTERIA TOLERATED UP TO AND INCLUDING 5% SALT
MOULDS (PENICILLIUM s.p.) TOLERATED UP TO AND INCLUDING 15% SALT
FILAMENTOUS YEASTS TOLERATED 2.5% SALT ONLY

DETERMINE SALT TOLERANCE OF DIESEL/RME POPULATION ADAPTED IN LABORATORY

FINDINGS

BACTERIA GROWING ON 0.2% RME/DIESEL TOLERANT OF 7.5%. BUT NOT 10% SALT

YEAST GROWTH ON 0.2% RME/DIESEL IMPROVED UP TO 7.5% SALT, BUT NOT 10% TOLERATED

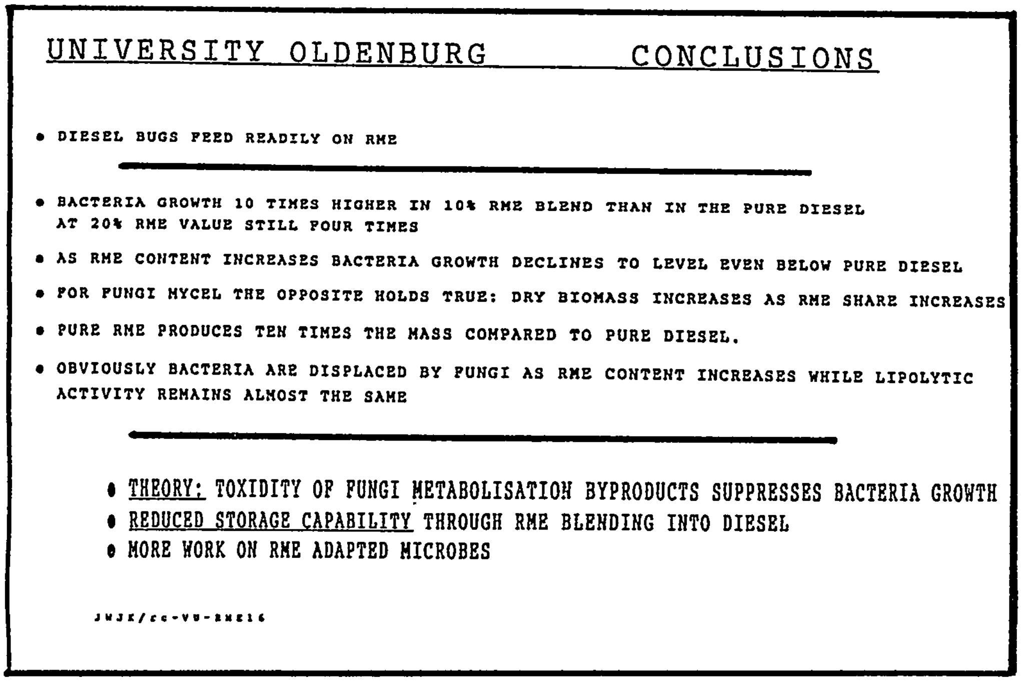
BACTERIA GROWING ON 20% RME/DIESEL TOLERANT TO 5% BUT NOT 7.5%, YEASTS WERE NOT TOLERANT AT ALL

MOULDS NOT TOLERANT OF ANY LEVEL

CONSEQUENCES FOR EBV SALT CAVERN STOCK MINIMAL

JWJK/cc-VU-RME27

Overall we concluded that there is no evidence that the danger is higher than with conventional diesel, whose tendency to harbour at brine interface proliferating bugs is very minimal indeed.



UNIVERSITY OLDENBURG CONCLUSIONS

- DIESEL BUGS FEED READILY ON RME

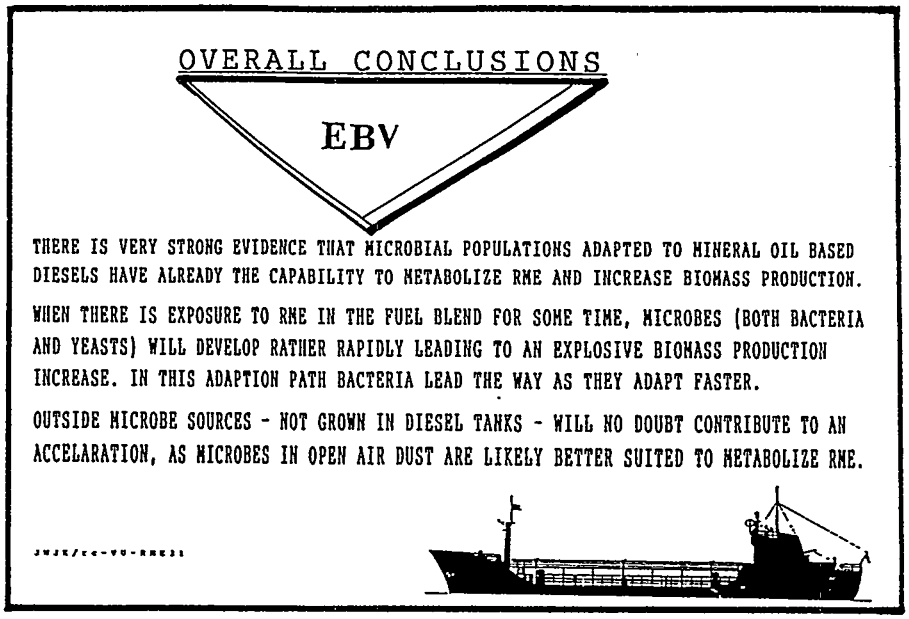
- BACTERIA GROWTH 10 TIMES HIGHER IN 10% RME BLEND THAN IN THE PURE DIESEL AT 20% RME VALUE STILL FOUR TIMES
- AS RME CONTENT INCREASES BACTERIA GROWTH DECLINES TO LEVEL EVEN BELOW PURE DIESEL
- FOR FUNGI MYCEL THE OPPOSITE HOLDS TRUE: DRY BIOMASS INCREASES AS RME SHARE INCREASES
- PURE RME PRODUCES TEN TIMES THE MASS COMPARED TO PURE DIESEL.
- OBVIOUSLY BACTERIA ARE DISPLACED BY FUNGI AS RME CONTENT INCREASES WHILE LIPOLYTIC ACTIVITY REMAINS ALMOST THE SAME

- THEORY: TOXIDITY OF FUNGI METABOLISATION BYPRODUCTS SUPPRESSES BACTERIA GROWTH
- REDUCED STORAGE CAPABILITY THROUGH RME BLENDING INTO DIESEL
- MORE WORK ON RME ADAPTED MICROBES

JWJK/cc-VU-RME16

It is worth briefly highlighting also the finding from the parallel study at Oldenburg University, which covered a wider range of RME/diesel blends. It was confirmed that at low RME concentrations bacteria grow much faster and produce more biomass than in conventional diesel. Bacteria growth however declines as the share of RME increases while fungi increase on account of bacteria keeping the lipolytic activity almost equal. The theory holds that metabolic by-products of fungi are toxic to bacteria and thus restrict their growth:

The overall conclusion can be formulated as follows



OVERALL CONCLUSIONS

EBV

THERE IS VERY STRONG EVIDENCE THAT MICROBIAL POPULATIONS ADAPTED TO MINERAL OIL BASED DIESELS HAVE ALREADY THE CAPABILITY TO METABOLIZE RME AND INCREASE BIOMASS PRODUCTION.

WHEN THERE IS EXPOSURE TO RME IN THE FUEL BLEND FOR SOME TIME, MICROBES (BOTH BACTERIA AND YEASTS) WILL DEVELOP RATHER RAPIDLY LEADING TO AN EXPLOSIVE BIOMASS PRODUCTION INCREASE. IN THIS ADAPTION PATH BACTERIA LEAD THE WAY AS THEY ADAPT FASTER.

OUTSIDE MICROBE SOURCES - NOT GROWN IN DIESEL TANKS - WILL NO DOUBT CONTRIBUTE TO AN ACCELARATION, AS MICROBES IN OPEN AIR DUST ARE LIKELY BETTER SUITED TO METABOLIZE RME.

JWJK/EE-VU-RME31

Having followed me all the way to this point with the largest concern about RME being a biological issue, allow me to end with these final words:

R M E

- TOO GOOD TO BE WASTED
  - AS ORDINARY DIESEL OR DIESEL BLEND
  - EVEN LESS IN HOME HEATING OIL
- PREMIUM FUEL AND LUBE
  - FOR SENSITIVE SITUATIONS
  - NEED FAST DEGRADATION
  - NEED AS OXIGENATE TO IMPROVE COMBUSTION
- COST JUSTIFIES PREMIUM NICHE APPLICATION ONLY

WRONG APPLICATIONS RUIN A PERFECT REPUTATION

RME is an excellent material of very limited and certainly not growing production capacity. It definitely has proven advantages over some mineral oil based products of similar characteristics even though many of the promises seem to be untrue or at least overrated. As a fuel it is cleaner but some exhaust emissions give rise to concern. Its high oxygen content increases fuel consumption in cars as oxygen has no heating value, though the oxygen like all oxygenates help the combustion and burner performance. The contribution to the reduction of "greenhouse" gases is questionable to non-existent. As a premium product it is too good to be wasted in diesel and heating oils as blendstocks, its use in sensitive situations where biodegardability is an advantage is undoubted and for "much-more" the availability of rape seeds will restrict the expansion in the long run as agricultural set-aside and waste land declines rapidly in the European Union and elsewhere and the food sector in Asia and Africa absorbs ever growing oil seed volumes. For long storage the RME is truly not suited due to the high biovulnerability and the preventive use of biocides for improving it cannot be supported on medical and environmental grounds.

So beware of wrong applications ruining the perfect reputation of a premium product.

Thank you for your patience ladies and gentlemen.

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6th International Conference
on Stability and Handling of Liquid Fuels
Vancouver, B.C., Canada
October 13-17, 1997

STORAGE STABILITY OF REFORMULATED GASOLINES (RFG)

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ABSTRACT

The Defence Fuel Supply Center (DFSC) is procuring reformulated gasoline (RFG) for storage aboard Military Prepositioned Ships (MPS). For DFSC's procurement of RFG, a time period extending to four years after time of acceptance is anticipated, with an average storage temperature assumption of approximately 20°C. The oxidation stability of the RFG using the standard induction period method (ASTM D 525) has been specified at a minimum of 480 minutes. Additionally, use of oxidation inhibitors over the range of 5 to 15 pounds per 1,000 barrels (PTB) of gasoline, and an approved metal deactivator at 1 to 3 PTB of gasoline are being required. An approved corrosion inhibitor may be added but is not required. While these additives have been previously developed and used over the past many years for conventional gasoline, their effectiveness in RFG has not been established. DFSC-supplied RFG and TFLRF(SwRI) formulated RFG blends (containing either MTBE, TAME, or ETBE) using a moderately stable gasoline blending stock, made unstable by the addition of dimethylhexadiene (DMHD) were evaluated for stability characteristics using test methods ASTM D 525 (Induction Test Method) and ASTM D 873 (Accelerated Gum Test Method) and the following additives: antioxidants (a phenylenediamine, a hindered phenol, and a 50/50 blend); metal deactivator; corrosion inhibitor ; deposit control additive. This data supports the suggestion that these additives were not antagonistically affected by the presence of any of the three ethers and formed a basis for recommending additive treatment rates. Based on previous Army evaluations, the washed gum limit was set at 5 mg/100mL as a maximum storage stability procurement guide for the D 873 8-hr test. In general, as a fuel ages, it develops higher intake valve deposit (IVD) capabilities which are measured indirectly by ASTM D 381 washed gum values and FTM 791C, Method 500.1 ISD appearance and mass values. When DFSC deposit control additive was added to base fuels in this program, they gave relatively low D 381 washed gum and were somewhat ineffective at 80 PTB for fuels which were probably dirtier than the reference fuel used to obtain the initial EPA qualification for this additive. In practice, the deposit control additive treat rate should be determined by D 381 testing for washed gum and ISD testing (both visual and mass of deposit) with neat and deposit control additive treated fuel.

BACKGROUND AND INTRODUCTION

DoD's continued use of some gasoline consuming military materiel/equipment, has required prepositioning of the newer Reformulated Gasolines and has prompted a DFSC sponsored investigation to assess the storage stability of these oxygenated fuels. For DFSC's procurement of RFG (DFSC procurement clause C16.18-1), a time period extending to four years after time of acceptance is anticipated, with an average storage temperature assumption of approximately 20°C. For this initial procurement, the oxidation stability of the RFG using the standard induction period method (ASTM D 525) has been tentatively specified at a minimum of 480 minutes. Additionally, use of oxidation inhibitors over the range of 5 to 15 pounds per 1,000 barrels (PTB) of gasoline, and an approved metal deactivator at 1 to 3 PTB of gasoline are being required. An approved corrosion inhibitor may be added but is not required. While these additives have been previously developed and used over the past many years for conventional gasoline, their effectiveness in RFG has not been established. This investigation makes use of previous data developed by the Army to demonstrate utility of using a 6-hr D 873 (ASTM Test Method for Oxidation Stability of Aviation Fuels), potential residue method, recommended for procurement of motor gasoline storable for four years in the NATO distribution system. The washed gum limit was set at 5 mg/100mL as a maximum for the D 873 6-hr test. This limit has been retained in the DFSC work; however, since the storage conditions are at higher temperatures than the NATO underground storage tanks, an 8-hr test time-period was utilized. (**Note**: All ASTM methods used in this work are available from ASTM Book of Standards, Part 5, 100 Barr Harbor Drive, West Conchohocken, PA 19428.)

The ASTM D 4814, "Standard Specification for Automotive Spark-Ignition Engine Fuel," provides a summary of U. S. Environmental Protection Agency (EPA) Regulations controlling fuel composition. In their "Regulation of Fuels and Fuel Additives; Standards for Reformulated and Conventional Gasoline, Final Rule," published in the 16 February 1994 Federal Register, it is mandated that RFG must meet three compositional requirements: 2.0 weight percent minimum oxygen, 1.0 volume percent maximum benzene, and no heavy metals (such as lead or manganese). For fuels containing aliphatic ethers and/or alcohols (excluding methanol), the maximum oxygen content allowed is 2.7 mass % oxygen, under the "Substantially Similar Rule," as summarized in Appendix X3 of ASTM D 4814. However, for fuels intended for long-term storage, based upon prior U.S. Army experience with GASOHOL, it has been recommended that only ether oxygenates be allowed, as the alcohols are more sensitive to moisture causing phase separation with the more dense water-alcohol mixture separating to the tank bottom. This is a serious matter when the alcohol represents as much as 10 percent of the fuel and the alcohol-water phase is a very poor performing gasoline. Ethers such as methyl tertiary-butyl ether (MTBE), tertiary-amyl methyl ether (TAME), and ethyl tertiary- butyl ether (ETBE) do not cause phase separation in the presence of excess water.

In the Clean Air Act Amendments of 1990, Congress specified that, beginning January 1995, all gasoline sold to the ultimate consumer in the U. S. must contain additives to prevent the accumulation of deposits in motor vehicle engines and fuel systems. For RFG procured for long-term storage, these detergent additives (i.e., deposit control additives) make predictive stability testing extremely difficult. Predicting the stability of gasolines fully formulated with deposit control additives (sometimes referred to as detergents in this paper) requires development of a new bench testing protocol which is not yet available.

A two-phase laboratory program to investigate the storage stability characteristics of both representative RFG samples being procured by DFSC and special laboratory formulated blends (containing either MTBE, TAME, or ETBE) to enable the optimum antioxidant and metal deactivator combinations to be determined for various ether-type oxygenates, has been completed.

DISCUSSION

Two each one-gallon Defense Fuel Supply Center-Reformulated Gasoline (DFSC-RFG) samples, labeled as Barge Sample (B) and Tank 3203 (Running Sample), were received and coded as AL-23899-G and AL-23900-G, respectively. A second set of samples were received and coded AL-23974-G and AL-23925-G, respectively. Table 1 contains a summary of data generated in the initial stages of this project.

TABLE 1. Summary of Initial Test Data

Test Procedure	Test Results				
	DFSC-RFG Samples			High Deposit Fuel	Reference Gasoline
	Procurement Requirement, C16.18-1 [or D 4814]	Tank 3203, Running Sample, AL-23900-G	Barge Sample B, Al-23899-G	PIFF Lot S-300, AL-23965-G	"J" Fuel, AL-20340-G
D 381, mg/100 mL					
Unwashed		5.0	9.2	93.1	2.8
Washed	[5, max]	0.3	1.8	7.8	2.3
D 525, minutes	480, min	675	690	>960	>960
D 873, mg/100 mL					
16 Hr (Modified)					
Unwashed		1253		175.4	8.5
Washed		1233		25.0	8.1
8 Hr					
Unwashed		29.8	42.0		
Washed		29.4	18.2		
6 Hr					
Unwashed		14.0	19.7		
Washed		10.9	8.3		
D 4815, M%(V%)		TFLRF: LAB 08:			
Methanol	0.0, max	0.0 0.0			
Ethanol	0.0, max	0.0 0.0			
MTBE		9.4 (9.5) 10.0(10.0)		0.1	0.4
ETBE		0.1 (0.1) 0.0(0.0)		<0.1	<0.1
TAME		0.4 (0.3) 0.4(0.3)		<0.1	<0.1
(Benzene, estimate)		1.3 (1.1) 1.2(1.0)		2.6 (2.3)	2.1 (1.9)
Oxygen	2.0, min [2.7, max]	1.8 1.9		<0.1	<0.1
D 3606, Vol %					
Benzene	1.0, max	0.8			1.5
Toluene	NR	1.5			17.2
D 4052					
Density, g/mL				0.7703	0.7667
Gravity, API				52.0	53.0

Since the Port Injector Fouling Fuel (PIFF) had a very high unwashed gum, a better base fuel was sought. The properties of Phillip's "J" reference gasoline were attractive. Addition of 2,5-dimethyl-2,4-hexadiene (DMHD) reduced the D 525 induction periods as shown in Fig. 1. A DMHD concentration of 2.5 V% was selected for the base gasoline.

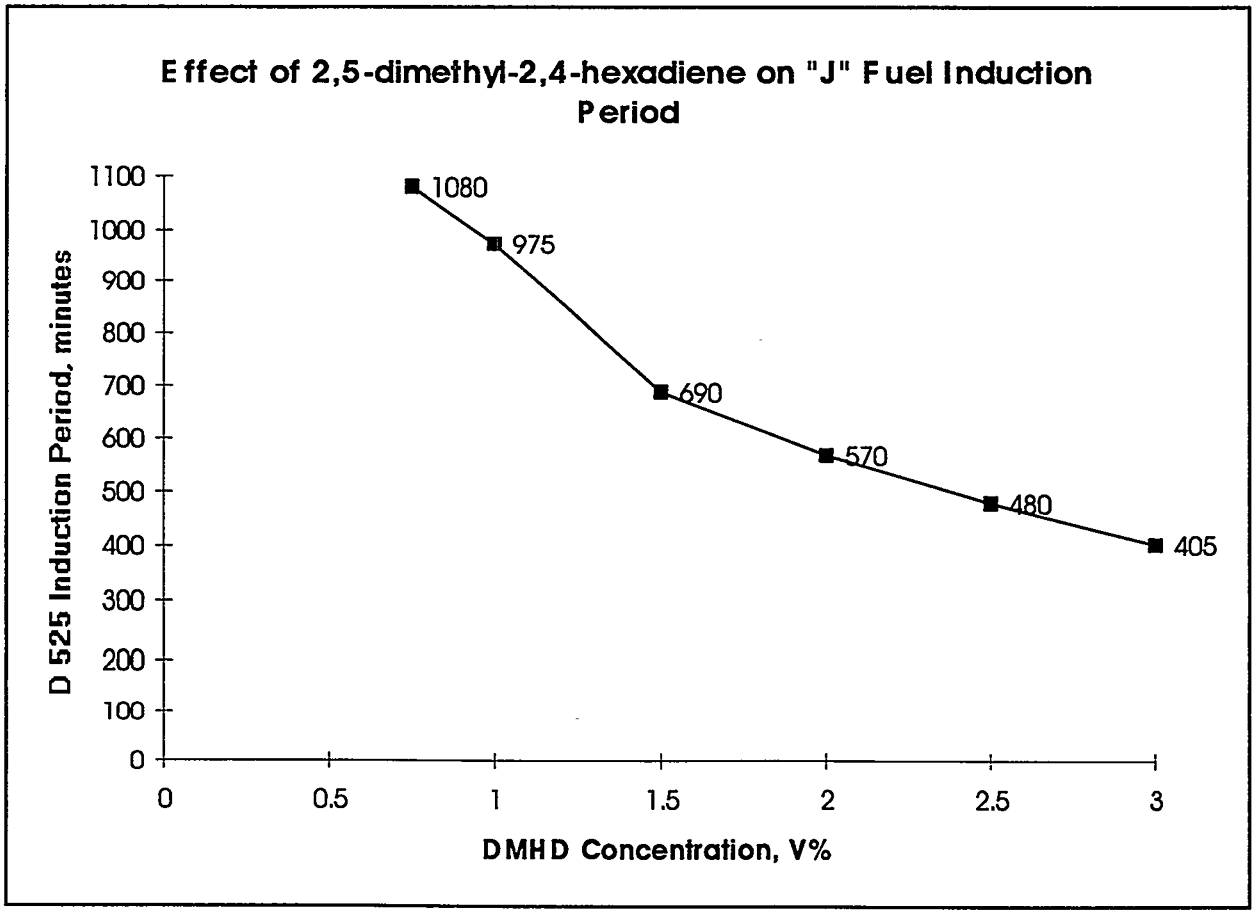

Figure 1. Effect of 2,5-dimethyl-2,4-hexadiene on "J" Fuel Induction Period

Since "J" fuel and Methyl tertiary-Butyl Ether (MTBE) stored over deionized water caused a haze when the wet MTBE was added to the wet "J" fuel, it was decided to use "J" fuel stored over a water bottom and add 50 percent wet and 50 percent dry ether to the volumetric concentration to give 2.7 mass percent oxygen for the three following ethers:

- methyl tertiary-butyl ether (MTBE): 15 V%
- tertiary-amyl methyl ether (TAME): 17 V%
- ethyl tertiary-butyl ether (ETBE): 17 V%

Since testing was to be done over an extended period of time, it was deemed best to minimize sources of chemically related instability. For example, the DMHD should be added to the test fuel on the day of testing, as opposed to mixing a batch of base fuel sufficient for making all of the samples. The DMHD contains 0.01 wt% stabilizer (Butyl Hydroxy Toluene abbreviated BHT which is 2,6-di-tert-butyl-4-methylphenol). Care was also taken after each use to more quickly flush the bottle's ullage with nitrogen. Epoxy-lined containers of antioxidant-treated "J" fuel were stored with water bottoms. For testing, these "wet" fuels would than receive DMHD and appropriate ether.

The rest of this discussion addresses data in Phases 1 & 2 as provided in Appendix 1 & 2 (available on request).

A. Phase 1 Data: Using AO22 (a hindered phenol) at minimum and maximum concentrations and varying the DMHD#1 from 1.5, 2.0 & 2.5 V% in J fuel containing 15 V% MTBE, the induction periods shown in Fig. 2 were obtained. The D 873 480-minute potential gum remains above 10 mg/100mL in Fig.2 even at induction periods in the 600 minute range. This data also demonstrates that a minimum induction period of 480 minutes is not a guarantee of a low potential gum at 480 minutes.

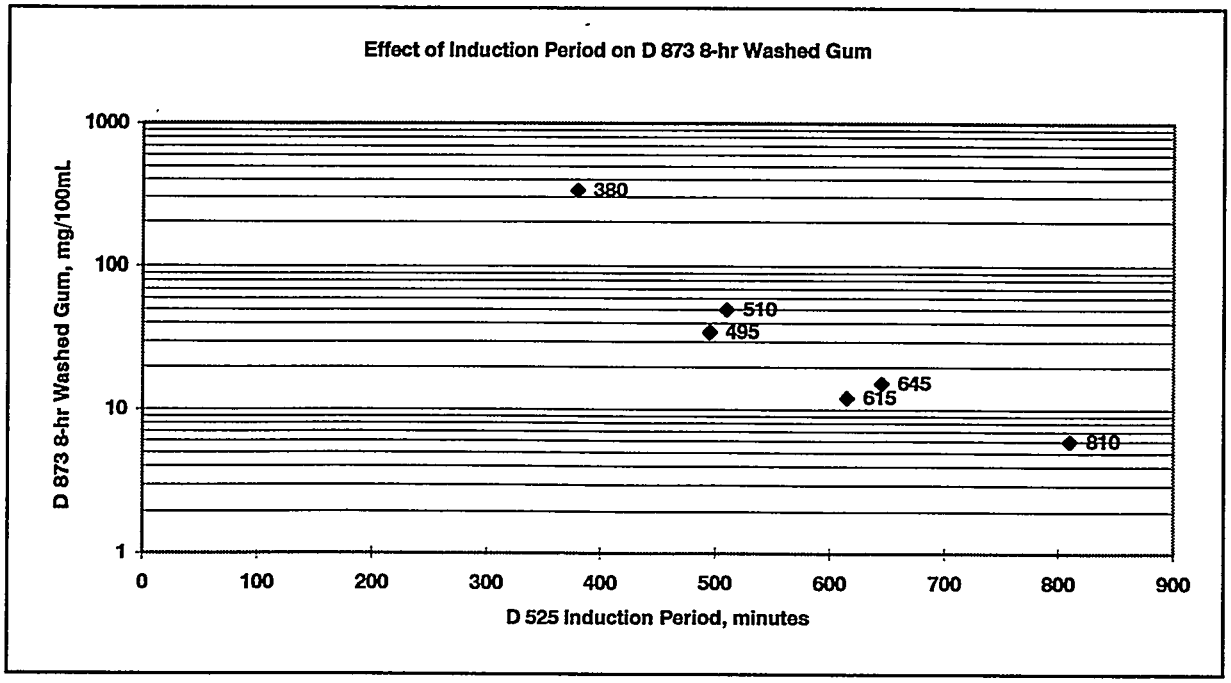

Figure 2. Relationship of induction period and potential gum for J-RFG (MTBE) fuel

Fig. 3 provides D 525 induction period data for unstable "J" fuel.

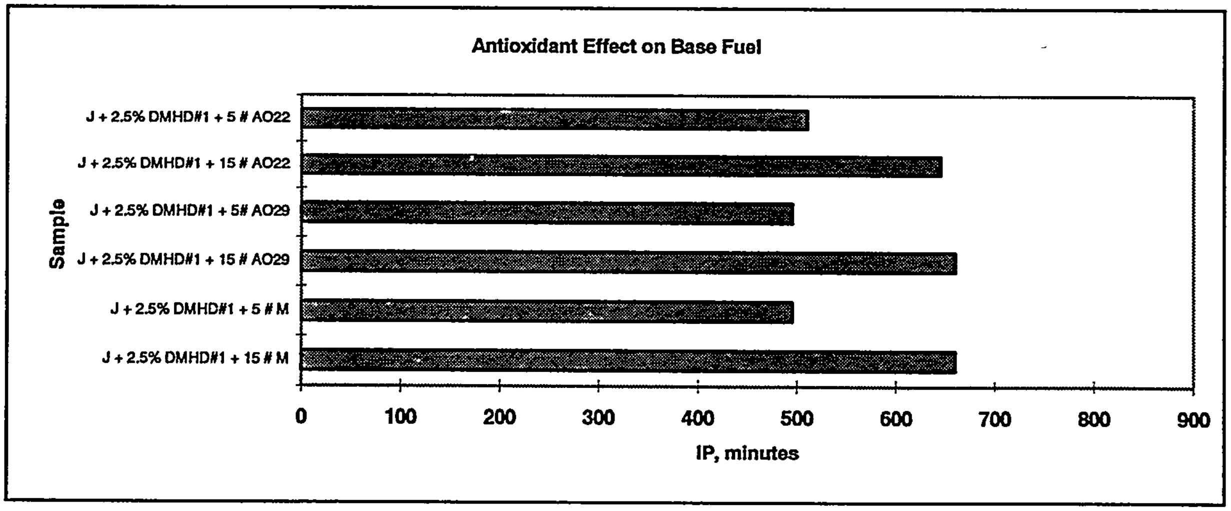

Figure 3. Induction period effect of antioxidants on unstable J fuel

Both the hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable "J" fuel as demonstrated in Fig. 3, using antioxidant treat levels of both 5# and 15# per thousand barrels of fuel.

Using MTBE in "J" fuel to make stable RFG (reformulated gasoline) and unstable RFG, referred to as J-RFG and unstable J-RFG (when containing DMHD), the data in Fig. 4 demonstrates the

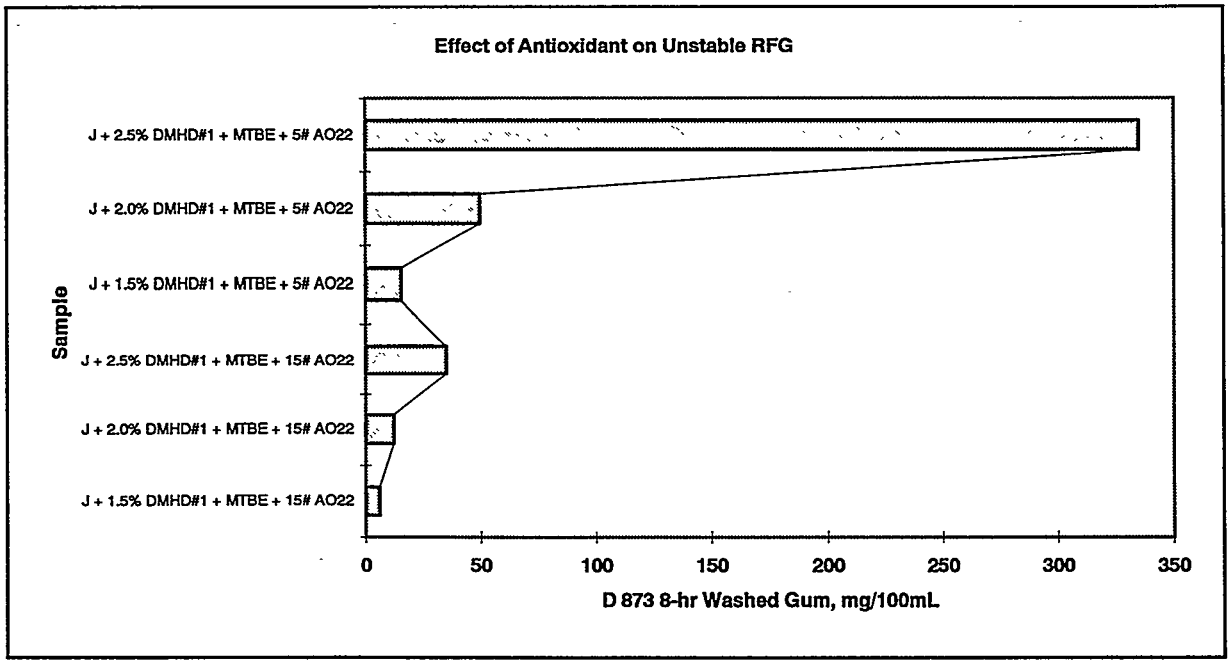

Figure 4. **Potential gum effect of antioxidant on various levels of unstable J-RFG (MTBE)**

relationship of AO22 concentration at two levels to DMHD unstabilizing effect at three concentrations. This same data was plotted against induction period in Fig. 2. In the range of 10 to 30 % in unstable J fuel, MTBE tends to increase the induction period while hexane decreases the induction period by up to 10 %. This is interpreted that the oxidation activity of the J fuel and the DMHD are decreased by ethers and enhanced by hexane (which is considered to be a stable hydrocarbon compared to more reactive olefins). Additionally, this suggests that MTBE and the ethers (in this project) do not readily autooxidize or participate in the autoxidation reactions, as might be expected since they already contain oxygen.

The effect of copper at 0.2 mg/L was reduced in the presence of MTBE, TAME, and ETBE. While copper dramatically reduces the induction period of J fuel, addition of the ethers, especially MTBE increases the induction period by about 150 minutes. Both Metal Deactivator numbers MD#2 and MD#75 are effective in nullifying the effect of copper (at a high concentration of 0.2 mg/L) independent of the presence of TAME, MTBE, or ETBE.

The effect of zinc (in the form of zinc naphthanate) was evaluated for its effect on induction period and potential gum. Zinc (over the range 0.6 to 2.4 mg/L) was ineffective in reducing the induction period of DMHD treated "J" fuel. This was also substantiated by D 873 8-hr potential gum. Zinc (from metal surfaces or zinc rich coatings) is well known for forming gelatinous precipitate with naphthenic acids in middle distillates, but has not been shown to catalyze oxidation reactions.

No dramatic effects of zinc were noted for the potential gum formed in unstable "J" fuel or unstable J-RFG (made using MTBE at 15 V%). As a check of the effect of deposit control additive, "D," on induction period, the data generated showed no effect.

The deposit control additive was ineffective in reducing the induction period of J-RFG (MTBE), metal deactivator stabilized copper contaminated (0.2 mg/L) "J" fuel, and unstable "J" fuel.

Fig. 5 provides induction period data to demonstrate the effectiveness of AO22, AO29, and a 50/50 mixture of the two antioxidants at two concentrations (covering the minimum and maximum of the procurement specification range) in unstable J-RFG (MTBE). Note that the instability of the J-RFG was varied by varying the concentration of DMHD#1. Day to day changes were noted in the reactiveness as time progressed, so a new bottle of DMHD (labeled DMHD#2) was used with more care in keeping it stable in its container, as explained earlier.

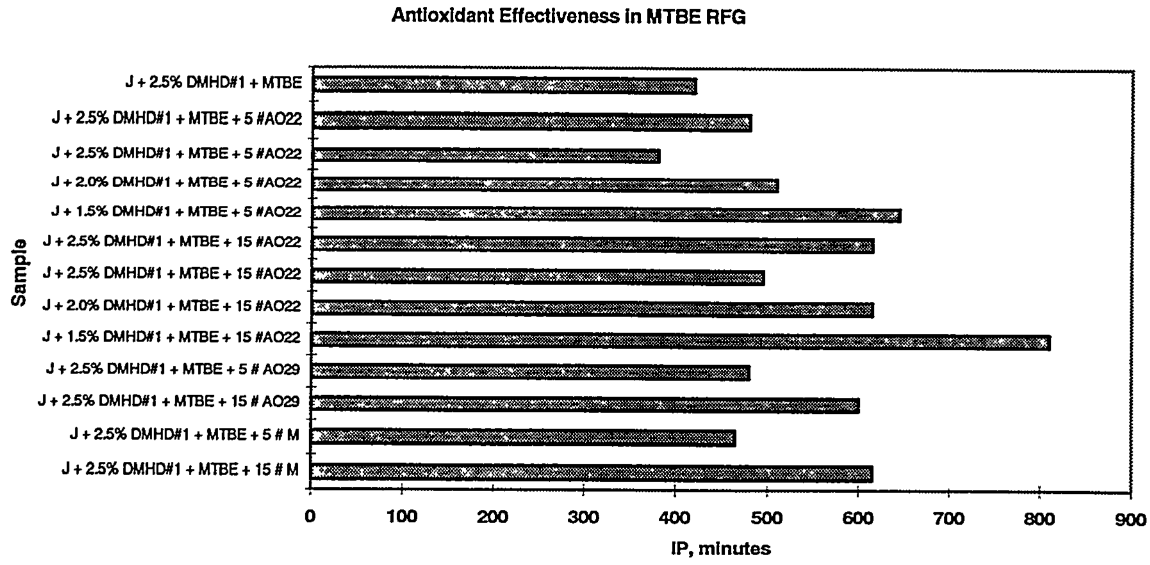

Figure 5. Induction period effect of antioxidants on unstable J-RFG (MTBE)

Some of the data in Fig. 5 (using DMHD#1) was used to demonstrate the relationship of induction period to potential gum using MTBE in unstable J fuel in Fig. 2.

Both the hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing MTBE.

Fig. 6 provides a dramatic demonstration of the stabilizing effect of AO22 at two concentrations in three levels of stability for unstable J-RFG, necessary to obtain a washed D 873 8-hr gum value of less than 5 mg/100mL.

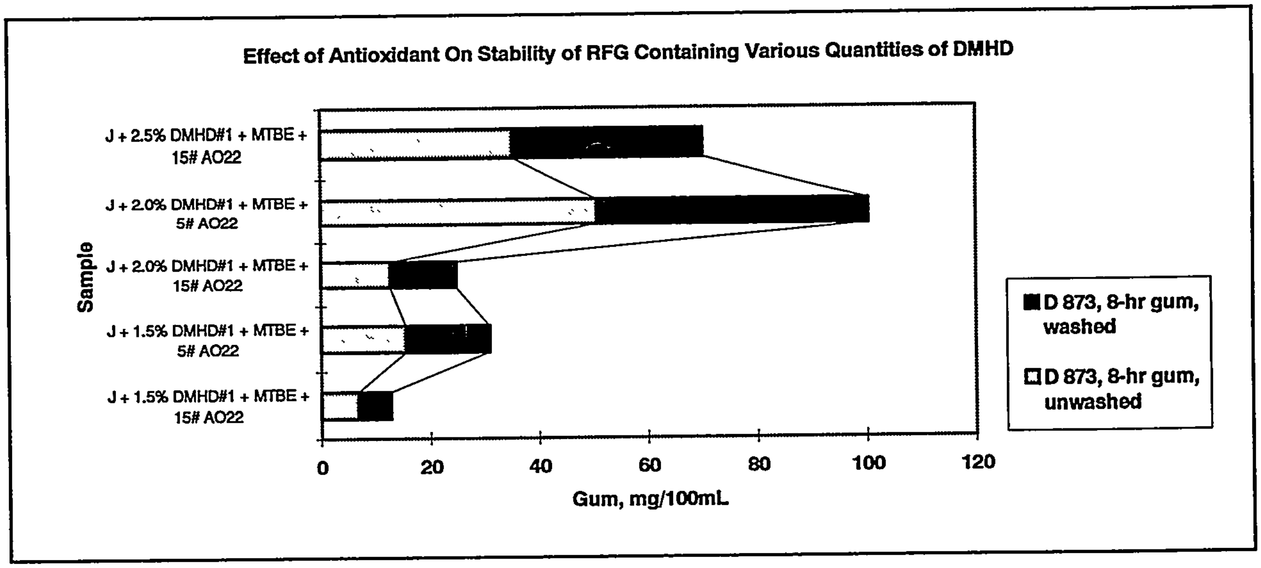

Figure 6. Potential gum effect of antioxidant on various levels of unstable J-RFG (MTBE)

For the relative stabilizing ability of AO22, AO29, and a 50/50 mixture of the two at the two concentration extremes for unstable J-RFG (MTBE), at the lower antioxidant concentration, AO29 is more effective than AO22. A similar effect was noted for induction periods of unstable J-RFG in Fig. 7.

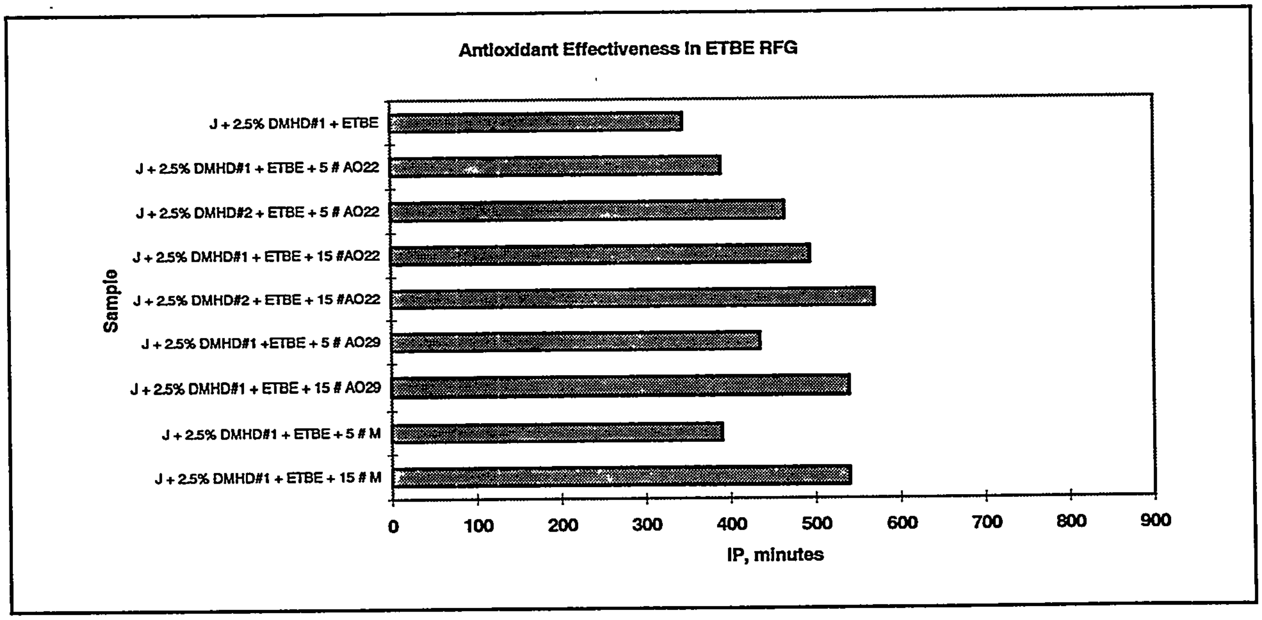

Figure 7. Induction period effect of antioxidants in J-RFG (ETBE)

Both the hindered phenol and the phenylenediamine as well as a mixture of the two are essentially equal in stabilizing unstable J-RFG containing ETBE, except that AO29 appears more potent at the lower treatment concentration.

The D 873 480-minute potential gum remains above 5 mg/100mL for the maximum treatment level which gave induction periods slightly above 500 minutes. This data also demonstrates that a minimum induction period of 480 minutes is not a guarantee of a low potential gum at 480 minutes. Similar data and observations were observed for unstable J-RFG (TAME). Both the hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing TAME.

After having extensively tested the "J" fuel, the DFSC-RFG obtained in the early stage of the project was subjected to similar testing to confirm conclusions drawn using the "J" fuel. Both the hindered phenol and the phenylenediamine and a mixture of the two were used at four concentration levels ranging from 0.5 to 15 pounds per thousand barrels. The AO22 was more effective in reducing the induction period than was AO29, in Fig. 8. Also, it appears that the phenylenediamine (AO22) is considerably more effective than the hindered phenol (AO29) at the lower treatment concentration, for reducing potential gum. Previous data has shown the effectiveness ratio of phenylenediamine to hindered phenol to increase from 2 at 10 % olefins to 8 at 50 % olefins (M.W. Schrepfer and C.A. Stansky, "Gasoline Stability Testing And Inhibitor Application," 1981 National Fuels and Lubricants Meeting, paper No. FL-81-79, November, 1981). This particular DFSC-RFG has 14.8 % olefins.

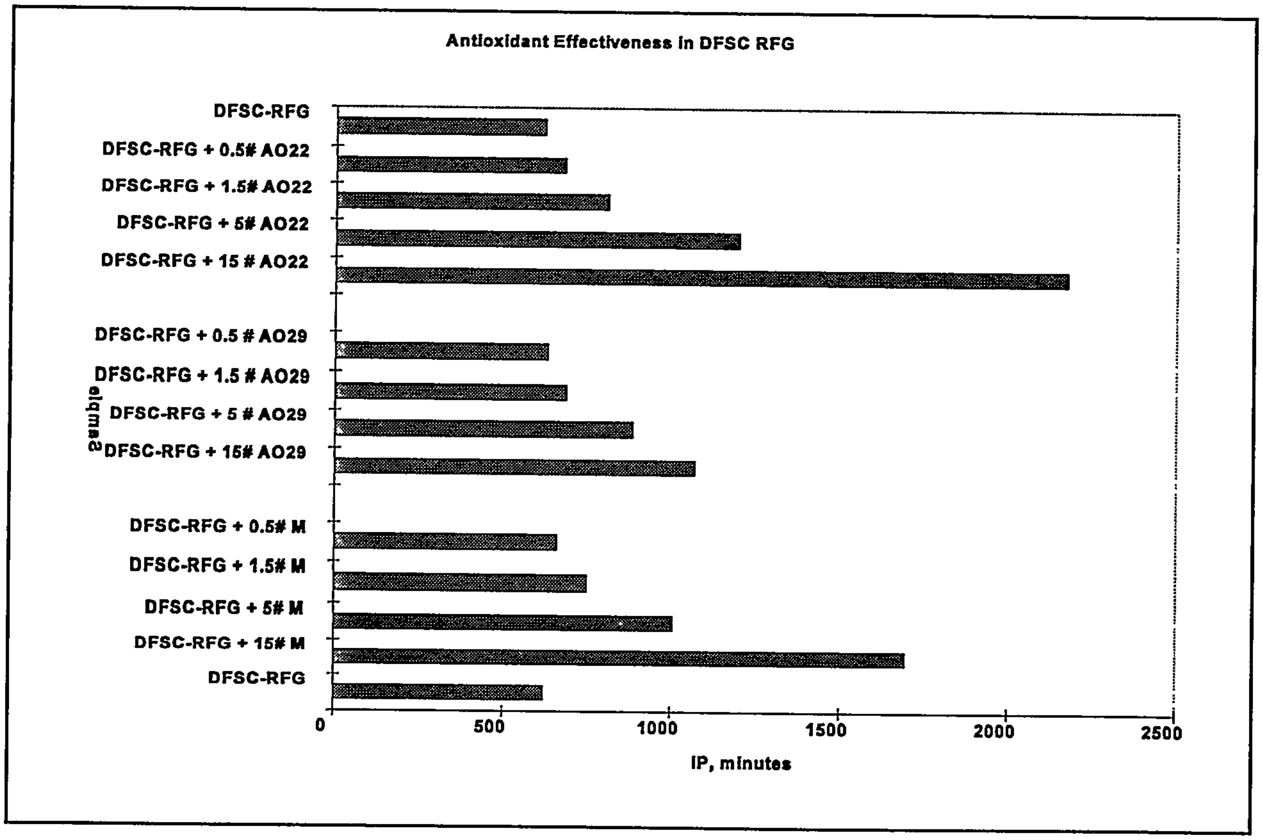

Figure 8. Induction period effect of antioxidants in DFSC-RFG

While copper significantly reduces the induction period for the DFSC-RFG, the metal deactivator at minimum concentration is effective in zeroing the copper effect, even in the presence of deposit control additive (D). While the D 873 8-hr potential washed gum is high, the deposit control additive was effective in reducing it to less than 2 mg/100mL. The metal deactivator was effective in the DFSC-RFG contaminated with copper (at 0.2 mg/L).

B. Phase 2 Data: The SwRI Intake Valve Deposit Apparatus (IVDA) (See SAE Paper No. 972838) was not sufficiently developed for use in this project. The Port Fuel Injector (PFI) test is currently in CRC-ASTM round robin evaluation and is supported by a wealth of data linking it to the injector fouling in the Crysler 2.2L engine. Selection of test injectors is a critical component of the bench test, thus injectors which foul in the vehicle are selected and retained for use in the bench test. It seems important that the injectors have a tendency to leak fuel slowly to give a deposit. If they leak too fast or not at all, deposits do not tend to form. The test developers state that additives that work well in the PFI test will generally work well in the BMW test. The 10,000 mile BMW vehicle IVD (Intake Valve Deposit) test continues as the basis for qualifying deposit control additives for use in gasoline by both CARB (California Air Resources Board) and EPA (Environmental Protection Agency). It is generally conceded that the dirtier (higher depositing) base fuels require higher concentrations of deposit control additives to maintain "Keep Clean" conditions on the intake valves. For deposit control additive, (coded "D" at the minimum effective concentration in this report), the current minimum effective "D" additive treatment level was 80 PTB (pounds per thousand barrels), or 224 mg/L. In general, as a fuel ages, it develops higher IVD depositing capabilities which are measured indirectly by ASTM D 381 washed gum values and FTM 791C, Method 500.1 ISD appearance and mass values. When DMA-452 was added to base fuels in this program, they gave relatively low D 381 washed gum and were somewhat ineffective at 80 PTB for fuels which were probably dirtier than the reference fuel used to obtain the initial EPA qualification. Other deposit control additives representing more recent technology were also evaluated obtaining similar results. Data was developed to establish the deposit control additive quality and relative response in aged fuel (added both prior to ageing and after ageing). This phase was limited to testing using D 381 and possibly ISD (Induction System Deposits) by Federal Test Method 500.1. A 600-mL reaction vessel was re-installed in the laboratory for use in 100°C ageing larger sample volumes in Phase II. This allowed for 8-hr aging 300 to 400 mL of test fuel per batch. The effect of deposit control additive (D) at the minimum effective rate and at both two and three times the minimum effective rate is to increase the unwashed D 381 gum and to decrease the washed D 381 gum in J-RFG (MTBE) fuel as demonstrated in Fig. 9.

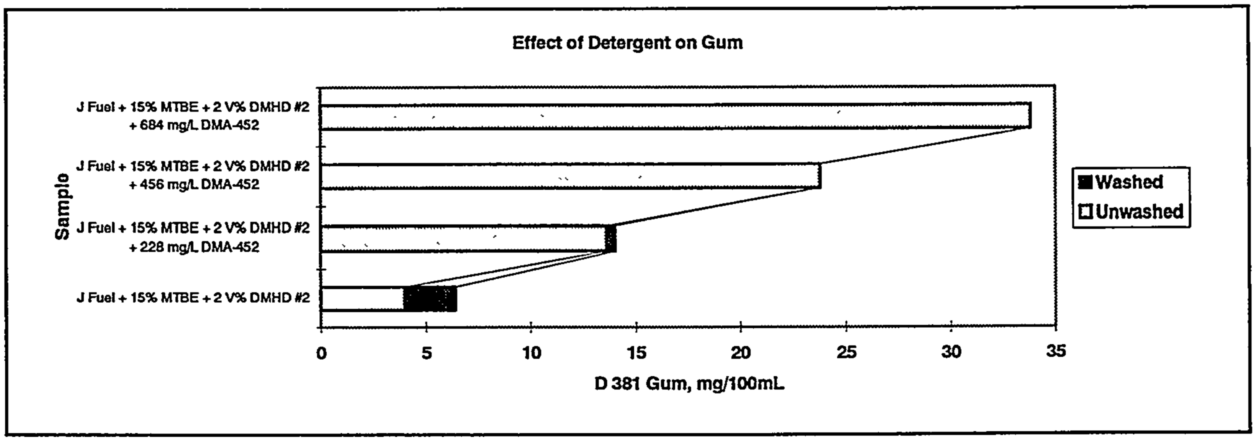

Figure 9. Effect of deposit control additive on D 381 gum in J-RFG (MTBE)

The effect of deposit control additive on potential gum in J-RFG (MTBE) is shown in Fig. 10. When the same fuels as in the Fig. 9 were submitted to D 873 8-hr potential gum testing, the deposit control additive was ineffective in reducing the washed gum, and actually appeared to increase the washed gum levels, as shown in Fig. 10.

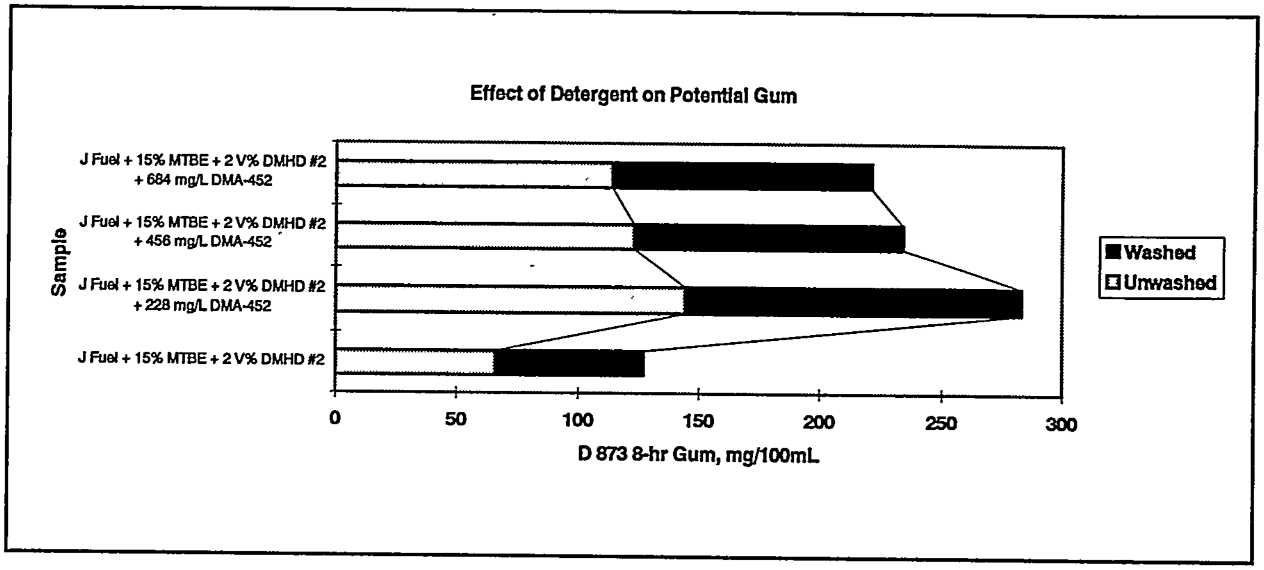

Figure 10. <u>Effect of deposit control additive on D 873 potential gum in J-RFG (MTBE)</u>

When the same DFSC-RFG fuels were submitted to D 873 8-hr potential gum testing, the deposit control additive was ineffective in reducing the washed gum, and actually appeared to increase the washed gum levels. Data showing the effect of aged unstable "J" fuel on D 381 gum levels in "J" fuel is provided in Fig. 11.

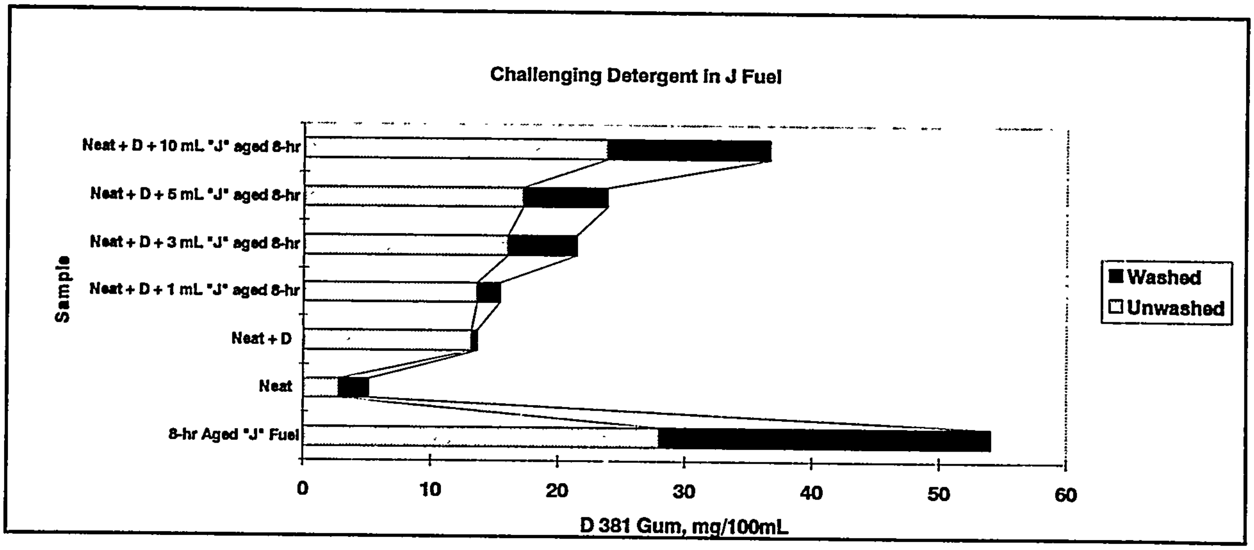

Figure 11. <u>Effect of aged unstable "J" fuel on D 381 gum levels in "J" fuel</u>

D 873 8-hr aged unstable "J" fuel (unstabilized by addition of 2 V% DMHD#2) gave a washed gum value of 26 mg/100mL. When this deteriorated fuel was added to neat "J" fuel containing deposit control additive (D) at the minimum effective treatment rate, the washed gum was dramatically effected by 3 mL of aged "J" fuel, which indicated the deposit control additive was overwhelmed by between 1 and 3 mL of the aged fuel.

This same effect was evaluated using the deposit control additive at double the minimum treat rate as shown in Fig. 12.

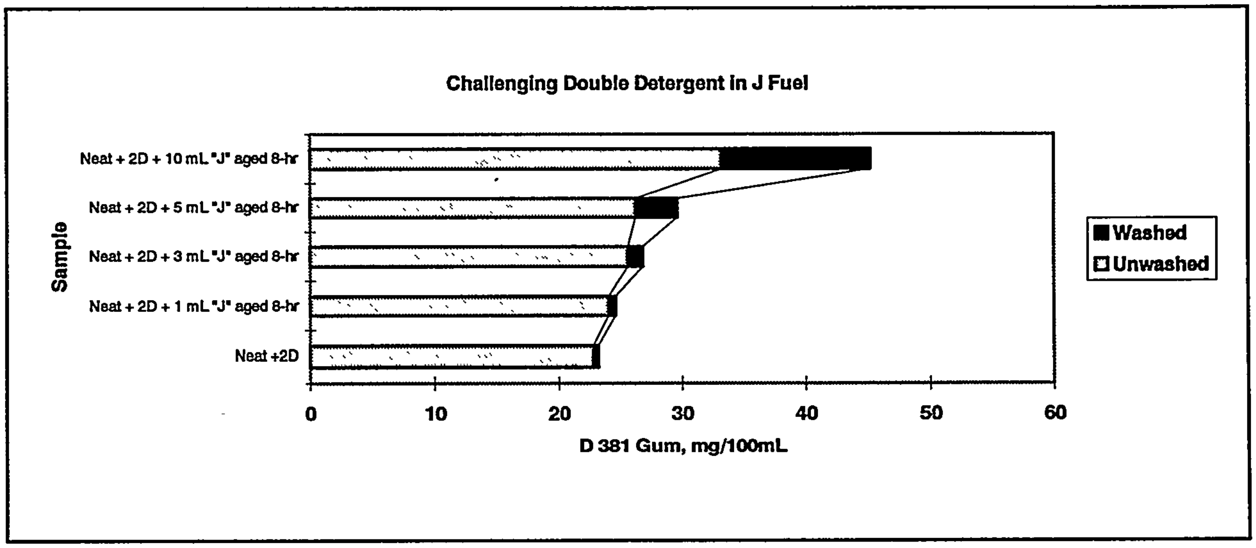

Figure 12. Effect of aged unstable "J" fuel on D 381 gum levels in "J" fuel

When this deteriorated "J" fuel was added to neat "J" fuel to which was added double detergent (2D), or twice the minimum effective rate, the washed gum was dramatically effected by 5 mL of aged "J" fuel, which indicated the deposit control additive was overwhelmed by between 3 and 5 mL of the aged fuel. This same approach was applied to the DFSC-RFG.

When the deteriorated unstable "J" fuel was added to neat DFSC-RFG fuel containing deposit control additive (D) at the minimum effective rate, the washed gum was dramatically effected by 5 mL of aged "J" fuel, which indicated the deposit control additive was overwhelmed by between 3 and 5 mL of the aged fuel. When the deteriorated "J" fuel was added to neat DFSC-RFG fuel containing double deposit control additive (2D), or twice the minimum effective rate, the washed gum was not dramatically effected even by 10 mL of aged "J" fuel, which indicated the deposit control additive was not overwhelmed by 10 mL of the aged "J" fuel.

In the Federal Test Method Standard No 791C, test method 500.1 is used to measure spark-ignition engine induction system deposit (ISD) potential of gasoline. The general level at which a gasoline is suspect of causing excessive ISD is 2 mg/100mL. Addition of deposit control additive to a high ISD fuel causes the deposit level to drop. While this method has been shown incapable of correlating directly to the 10,000 mile vehicle engine test to provide a ranking of the relative effectiveness of different deposit control additives, it does provide an indication of deposit control additive effectiveness when ISD values are very low or zero and the test tube has been observed to wash clean of deposit. Fig. 13 provides ISD data for the DFSC-RFG with varying quantities of aged "J" fuel added to it.

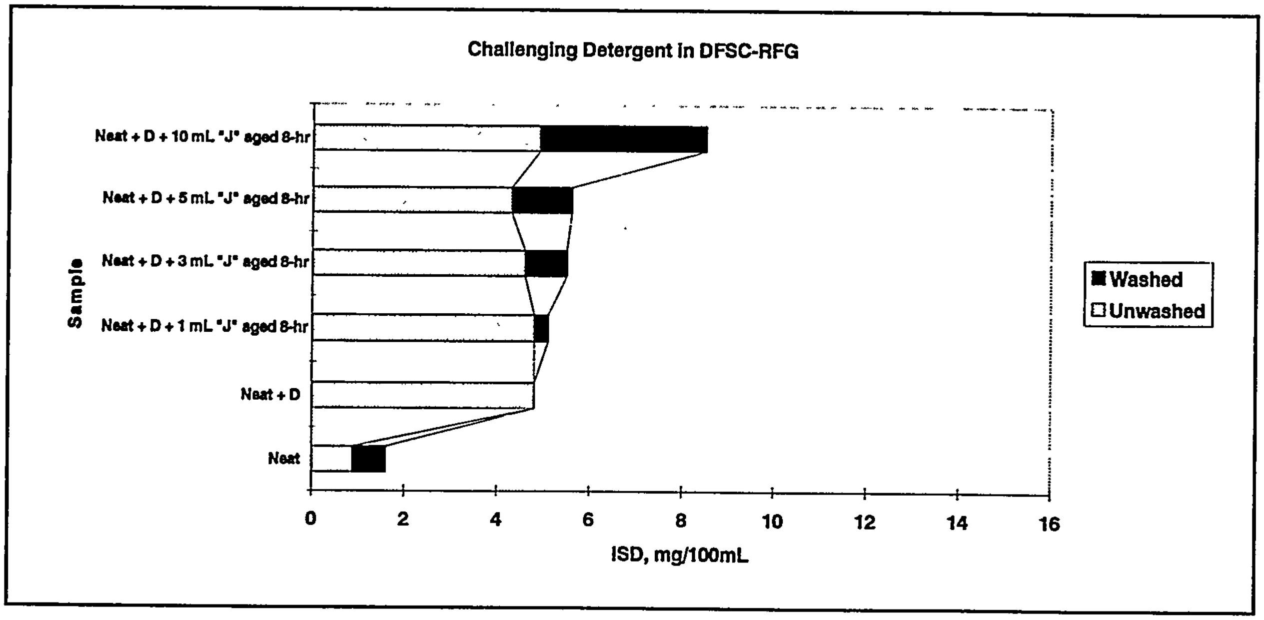

Figure 13. Effect of aged unstable "J" fuel on ISD levels in DFSC-RFG fuel

As little as 3 mL of aged "J" fuel caused a significant increase in the ISD for the DFSC-RFG fuel containing the minimum effective deposit control additive (D). When the deteriorated "J" fuel was added to neat DFSC-RFG fuel containing double deposit control additive (2D), or twice the minimum effective rate, and tested for ISD, as shown in Fig. 14, the deposit control additive was

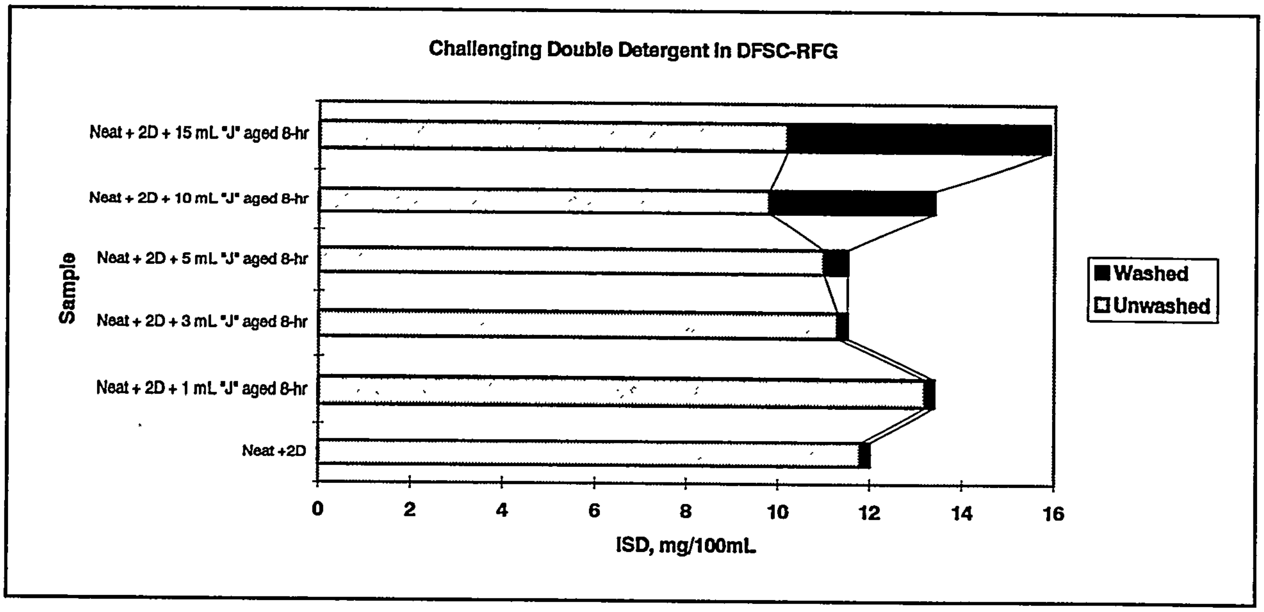

Figure 14. Effect of aged unstable "J" fuel on ISD levels in DFSC-RFG fuel

overwhelmed at 10 mL addition of aged "J" fuel and greatly overwhelmed at 15 mL addition of aged "J" fuel. In terms of engine induction system valve deposits, fuels with ISD values higher than 2 mg/100mL are considered high depositing fuels. The deposit on the test tube narrows as the deposit control additive becomes less effective as is demonstrated in the deposit appearance in the photograph of the test tubes, before and after washing with normal heptane.

In order to verify the results of challenging the DFSC-RFG deposit control additive with aged "J" fuel, the DFSC-RFG fuel was aged for 8-hr under D 873 conditions. This produced an aged fuel showing about 12 mg/100mL of washed D 381 gum compared to about 1 mg/100mL in the neat fuel. This aged DFSC-RFG was than added to 50 mL of DFSC-RFG fuel in quantities of 1, 3, 5, and 10 mL with the deposit control additive at two concentrations, D and 2D, the minimum effective concentration and double the minimum effective concentrations.

At the minimum effective concentration, the washed D 381 gum became high with the addition of 10 mL of aged DFSC-RFG. This means the deposit control additive was overwhelmed by between 5 and 10 mL of aged DFSC-RFG. When the deposit control additive was added at twice the minimum effective concentration, designated "2D", the washed gum remained low for all additions of aged DFSC-RFG including the 10 mL addition. To verify the deposit control additive challenge level for washed gum control was applicable to ISD levels, two samples were tested as shown in Fig. 15. Note the significant increase in ISD (approximately 2 mg/100mL) when 10 mL of aged DFSC-RFG was added to the DFSC-RFG fuel containing the minimum effective concentration of 228 mg/L ("D").

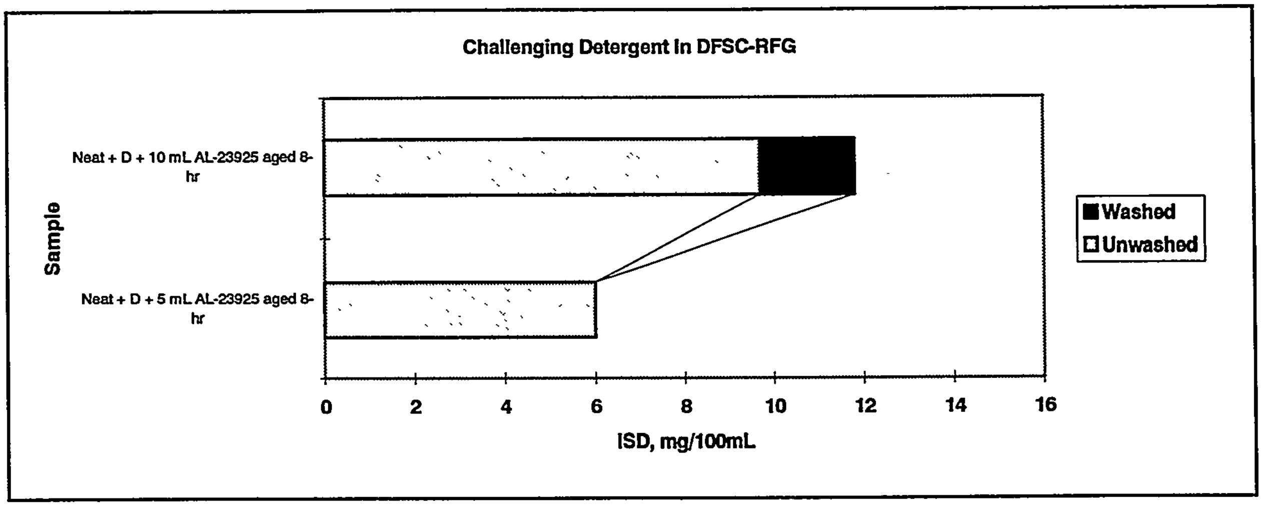

Figure 15. <u>Effect of aged unstable "J" fuel on ISD levels in DFSC-RFG fuel</u>

This data leads to the conclusion that the DFSC deposit control additive may need to be used at a higher concentration to be effective on aged DFSC-RFG and that the gum and ISD levels and deposit control additive response should be tested prior to deposit control additive addition.

While routine sampling of the MV HAUGE ship gasoline storage tank was accomplished and samples were analyzed for deterioration, summarized in Table 2, other stored fuel having additive was analyzed on a limited basis.

Table 2. Summary of Data for DFSC-RFG Samples Stored On Military Prepositioned Ships

Sample	D 525, minutes	D 381, Unwashed, mg/mL	D 381, Washed, mg/mL	D 873 8-hr, Unwashed, mg/mL	D 873 8-hr, Washed, mg/mL
MV HAUGE, Barge Sample B, AL-23899-G, 15 September 1995	690	9.2	1.8	42.0	18.2
MV HAUGE, 10 July 1995	>480	8.5	0.8	29.2	12.7
MV HAUGE, 05 August 1995	690	6.0	1.0	21.0	14.9
MV HAUGE, 04 November 1996	NA*	8.9	3.1	48.8	45.2
MV HAUGE, 05 January 1997	NA	10.5	2.9	NA	NA
MV HAUGE, 19 April 1997	NA	9.5	4.2	NA	NA
MV HAUGE, 15 March 1997	NA	13.7	3.1	NA	NA
MV PHILLIPS, From BC#110, 11 September 1995	1,575	3.4	0.7	7.1	5.7
MV PHILLIPS, 05 February 1997	1,560	10.0	2.3	11.8	5.8
Ship Unknown Barge # BC-110 21 January 1996	1,485	2.8	0.8	5.0	4.5

* NA = Not Available

While the unadditized fuel in the MV HAUGE did not exceed the D 381 washed gum specification limit of 5.0 mg/100 mL, it was very high at the time of replacement in June 1997. The additized fuel in the other two ships had lower gum and considerably lower D 873 8-hr gum at or near the recommended limit of 5 mg/100mL, at the time of initial filling. Only one sample from the MV PHILLIPS was received about 18-months of storage, and showed some ageing. No other surveillance samples were received from other MPS ships.

VI. SUMMARY AND CONCLUSIONS

This project was accomplished in two phases. Phase 1 covered the storage stability assessment of DFSC-supplied RFG with additive package outlined in C16.18-1 and without additive package.

TFLRF(SwRI) formulate three RFG blends using a moderately stable gasoline blending stock, obtained by the use of a reference fuel to which was added unstable DMHD. The ethers (MTBE, TAME, and ethyl tertiary-butyl ether (ETBE)) were used at volume percents to provide the oxygen content of 2.7 mass percent.

DFSC-supplied RFG with and without additive package were evaluated for stability characteristics using test methods ASTM D 525 (Induction Test Method) and ASTM D 873 (Accelerated Gum Test Method). Similarly, SwRI-formulated RFG were evaluated using the following additives:

- Antioxidants (required by Clause 16.18-1)
  - One phenylenediamine
  - One hindered phenol
  - 50/50 blend of above antioxidant additives
- Metal deactivator (required by Clause 16.18-1), both of the two approved formulations
- Corrosion inhibitor (not mandatory)
- Deposit control additive (mandatory for ultimate distribution of RFG but not required by clause 16.18-1 for long-term storage).

Phase I analyses support the suggestion that the additives which were evaluated were not antagonistically affected by the presence of any of the three ethers.

Fuel samples were formulated with varying concentrations of antioxidant. Using ASTM D 525 and ASTM D 873 8-hr gum date the following observations were made:

- The hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable “J” fuel, using antioxidant treat levels of both 5# and 15# per thousand barrels of fuel.
- In the range of 10 to 30 % in unstable J fuel, MTBE tends to increase the induction period while hexane decreases the induction period.
- The hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing MTBE. Similar effects was noted for induction periods and potential gum of unstable J-RFG.
- Both the hindered phenol and the phenylenediamine as well as a mixture of the two are essentially equal in stabilizing unstable J-RFG containing ETBE, except that AO29 appears more potent at the lower treatment concentration. The D 873 480-minute potential gum remained above 5 mg/100mL for the maximum treatment level which gave induction periods slightly above 500 minutes. This data also demonstrates that a minimum induction period of 480 minutes is not a guarantee of a low potential gum at 480 minutes. Similar data and observations were observed for unstable J-RFG (TAME)
- The hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing TAME

The effectiveness of corrosion inhibitor was measured using the ASTM D 130 (Copper Corrosion test method) and ASTM D 665 (NACE test). The presence of 15 V% MTBE, 15 V% TAME, or 17 V% ETBE in unstable J-RFG had no negative effect on the ability of corrosion inhibitor to prevent rust or copper corrosion.

The effectiveness of the two metal deactivator additives (MD#2 and MD#75) were found to be effective in neat reference fuel, J-RFG, and DFSC-RFG when contaminated with copper and were not adversely affected by the presence of detergent.

Zinc (organically compounded) was found to have no effect on instability even at 2.4 mg/L or in the presence of 15 V% MTBE in reference fuel. This was also substantiated by D 873 8-hr potential gum.

Since all RFG formulations require a detergent in final distribution, limited samples were also made with two different types of deposit control additives including the DFSC selected detergent, to determine effects on stability.

The DFSC deposit control additive was ineffective in reducing the induction period of J-RFG (MTBE), metal deactivator stabilized copper contaminated (0.2 mg/L) "J" fuel, and unstable "J" fuel.

The results with DFSC deposit control additive in the fuel were not completely conclusive in that accelerated testing did not always produce low washed gums. It seems best to recommend against accelerated testing of marginally stable fuels containing detergent, if possible, and evaluating addition of deposit control additive to either stored fuel or accelerated aged fuel for determining efficacy. This was addressed in phase 2 of this project.

In Phase II, the useability of RFG'S exposed to storage aboard military prepositioned ships (MPS), was to be addressed. Since no RFG's have been previously stored in MPS, the first DFSC-supplied RFG (Phase I) and the base fuel from Phase I (limited to MTBE as the oxygenate) were used in this phase. Testing included gum and ISD (Intake System Deposits) type testing to identify usability.

In general, as a fuel ages, it develops higher IVD depositing capabilities which are measured indirectly by ASTM D 381 washed gum values and FTM 791C, Method 500.1 ISD appearance and mass values.. When Deposit control additive was added to base fuels in this program, they gave relatively low D 381 washed gum and were somewhat ineffective at 80 PTB for fuels which were probably dirtier than the reference fuel used to obtain the initial EPA qualification.

Data was developed to establish the deposit control additive quality and relative response in aged fuel (added both prior to ageing and after ageing).

Testing to confirm adequacy of DFSC RFG's detergency requirement, for use in CONUS, suggested that use of DFSC deposit control additive may require higher treat rates than the minimum EPA effective treat rate. In practice, the treat rate should be determined by D 381 testing for washed gum and ISD testing (both visual and mass of deposit) with neat and deposit control additive treated fuel.

Information on vapor control in shipboard storage vessels and above-ground storage tanks, related to recommendations regarding long-term storage, were not available.

VII. RECOMMENDATIONS

Based on the data and discussions developed in this project, the following recommendations are made for use of additives in DFSC-RFG:

1. Do not require the presence of deposit control additive in gasoline for long-term storage. Actually, it is recommended that procurement clause C16.18-1 state that the gasoline not contain deposit control additive. Addition of DFSC deposit control additive is recommended at twice the minimum effective treatment during final distribution for use in CONUS and possibly OCONUS if the fuel deteriorates sufficiently to warrant its use.

2. Maintain D 525 limit at 480 minutes, minimum in procurement clause. Consider addition of D 873, 8-hr limit of 5 mg/100 mL increase in washed gum, maximum, to procurement clause.

3. Add Antioxidant and Metal Deactivator at the maximum treat rates.

ACKNOWLEDGEMENTS

This work was performed by the U.S. Army TARDEC Fuels and Lubricants Research Facility (TFLRF) located at Southwest Research Institute (SwRI), San Antonio, TX, during the period June 1995 through January 1996 under Contract No. DAAK70-92-C-0059. The work was jointly funded by the Defense Fuel Supply Center, Fort Belvoir, VA, and the U.S. Army TARDEC, Mobility Technology Center-Belvoir (MTCB), Fort Belvoir, VA. Mr. T.C. Bowen (AMSTA-RBFF) of MTCB served as the contracting officer's representative and project technical monitor.

6th International Conference
on Stability and Handling of Liquid Fuels
Vancouver, B.C., Canada
October 13 - 17, 1997

SUMMARY FINDINGS OF THE PROPERTY/COMPOSITIONAL RESULTS OF A WORLDWIDE COMMERCIAL MARINE DISTILLATE FUEL SURVEY

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Abstract

The Defense Fuel Supply Center, U.S. Navy and U.S. Army jointly managed the conduct of a survey of commercial distillate marine fuels and ground vehicle distillate fuels from forty-one locations around the world, including the continental United States. The type of samples sought were diesel fuels, 100-percent distillate (containing no residual) that are available in the commercial marketplace. Fuel sample collection was initiated in June 1996, and completed in October 1996. Over 2700 analytical results were obtained from the survey. This paper summarizes the extensive analytical data obtained including an interpretation of the results.

Background

The Mobility Fuels Group of the Carderock Division of the Naval Surface Warfare Center (NSWCCD) conducts studies to establish fuel property tolerance limits for Navy shipboard primary combustion and fuel handling equipment. A major effort of this group is to assess the impact that fuel property differences between commercial distillate marine fuels and fuels which meet military specifications would have on the performance and durability of shipboard equipment.

A survey of the properties of commercial fuels was conducted in 1985/1986 by collecting fuel samples from thirty overseas commercial locations. Samples of Marine Gas Oil (MGO), Heavy Marine Gas Oil, and Marine Diesel Fuel were gathered and analyzed. Information on fuel crude source, refinement and delivery history was also sought through questionnaires presented to the refiners when the samples were drawn. The results of this survey were used to establish the ranges of fuel properties to be used in determining the fuel property tolerance limits of high-speed diesel engines and gas turbine engines. The results of studies of the fuel property tolerance of high-speed diesel engines were used as the basis for broadening certain fuel property limits of Military Specification MIL-F-16884J, Fuel, Naval Distillate (NATO F-76).

In 1994, the office of the Under Secretary of Defense for Acquisition and Technology issued a directive to reduce the use of military specifications, where feasible, as a cost savings to the Federal Government. In response to this directive, the Defense Fuel Supply Center (DFSC) established a commercial specification initiative. In support of this initiative, the 1996 Worldwide Survey of Distillate Fuel was undertaken as a joint project with DFSC, the US Navy and the US Army. DFSC and Navy goals were to assess the degree to which distillate fuels available in the global commercial marketplace could be used aboard Navy ships. An additional Navy goal was to provide guidance to on-going studies whose goals are to determine engine/fuel tolerance limits. Army participation was aimed at obtaining a broadened range of distillate fuel samples from overseas sources for use in the development of a near-infrared technique for the analysis of fuel properties.

For the 1996 survey the American Bureau of Shipping (ABS) Marine Services Division and Oil Testing Services Division was contracted to contact refiners at Government specified sites, to interview refiner personnel and collect information for a questionnaire on refinery/terminal capabilities and practices, to obtain five-gallon samples of two different distillate fuels, and to ship these samples to a Government receiving site. Upon receipt, the samples were divided, one for analyses performed by the Army and the other for analyses performed by the Navy. This paper focuses on the analyses performed by the Navy and the findings derived from those analyses.

Sample Sites

The sites where fuel samples were to be obtained were selected by a committee composed of representatives of DFSC, NSWCCD, the Naval Research Laboratory (NRL), and the US Army Mobility Technical Center Belvoir. All sites selected were port cities where it was expected that both marine fuels and ground vehicle fuels would be available. Another criteria for selection was whether the site had been included in the survey conducted by NSWCCD in 1985/1986. Some sites were selected because they were included in the earlier surveys and would permit some comparisons, while others were selected to expand the number of locations covered. A third criteria for selection was whether DFSC and/or the Navy had purchased fuel at the site before. Some sites were selected because they were established points of supply and a comparison of available commercial fuel properties with those of military specification fuel was desired. Other sites were selected because DFSC and/or the Navy had never procured fuel there before and wished to inspect the fuels available. The thirty-three overseas sites and eleven sites in the United States that were selected for the 1996 Worldwide Survey of Distillate Fuels are listed in Table 1.

Fuels Sampled

The fuels sampled were identified by the following definitions:

Marine Gas Oil (MGO) - a middle-distillate fuel containing no residual fuel (i.e. 100% distillate) or dyes and is produced from petroleum crude and has a minimum flash point of 60°C as measured by ASTM D 93 or equivalent method. It is typically intended for use in off-highway and marine diesel engines.

Ground Vehicle Diesel Fuel (GVDF) - a middle-distillate fuel containing no residual fuel (i.e. 100% distillate) or dyes and is produced from petroleum crude. It is typically intended for use in ground vehicles and equipment powered by diesel engines. This fuel is similar to Grade Number 2-D of ASTM Specification D 975. It is also similar to US Defense Logistics Agency Commercial Item Description A-A-52557 which has replaced Grade DF-2 of former Federal Specification VV-F-800D. However, for the purposes of this survey it is not limited by these specifications.

At all sample sites, it was emphasized that the desired fuel was to be a commercial product rather than either a fuel made to military specifications or a custom-blended commercial product.

Sample Size

A five-gallon sample of both MGO and GVDF was sought at all sampling sites not in the United States. At those overseas locations where only one grade of distillate fuel was available, two, five-gallon samples of the same fuel were taken and labeled accordingly. At sampling sites in the United States, only samples of MGO were sought since the Army already had an extensive data base of domestic distillate fuel properties.

The relatively large 5-gallon sample size was chosen to provide sufficient sample to conduct property analyses as required in military specifications, and for use in such other fuels studies as Navy fuel lubricity tasks underway at Southwest Research Institute (SwRI), and in fuel storage stability tasks, fuel filterability/particulate contamination tasks and fuel cold flow property work underway at NRL. Fuel remaining after completion of this work was placed into cold storage at NRL for future use.

Five-gallon samples of fuel were obtained at all but one of the sites which permitted sampling. Local regulations in Kenya limited total sample size to four liters and limited shipping container size to one liter capacity. Consequently, two, four-liter samples of distillate fuels contained in a total of eight, one-liter bottles were obtained at this location.

Sample Gathering

ABS agents, working at their Roselle, New Jersey, USA office, made initial contact with the refiners, obtained permission to collect the fuel samples, arranged for on-site agents, shipped standardized sampling/shipping kits and questionnaires to the on-site agents, tracked the sample shipments and resolved shipping problems as they arose. Where possible ABS personnel performed as on-site agents, scheduling and supervising the drawing of samples, interviewing refinery personnel, mailing the completed questionnaires to the ABS office in Roselle, New Jersey, and shipping the samples to the receiving site. Where local restrictions and/or personnel availability did not permit the use of ABS personnel, local marine inspectors were subcontracted by ABS to perform the on-site agent function.

The sample containers used were new 5-gallon, epoxy-lined tighthead drums which met the requirements of ASTM Standard Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination, D 4306. They were approved by the International Air Transportation Association (IATA) as single packaging, rated UN 1A1/X 1.5/300/96 USA/VL, and also met the requirements of IATA's Dangerous Goods Regulations, Packaging Instruction 309. These drums were considered adequate for air shipment of distillate fuel samples at all locations.

The drums were shipped in fiberboard overpacks to provide additional protection. In practice, however, the use of the fiberboard overpacks caused significant confusion at overseas transshipment points where this packaging was often misinterpreted as combination packaging. Sample shipments were often delayed for several weeks while the adequacy of the drum/overpack packaging was resolved with local officials. All samples were received in good condition even though many arrived without the overpacks. The extra protection of the fiberboard overpack did not appear to be warranted, especially since delays could have been avoided if the drums had been shipped without them.

ABS successfully obtained samples from thirty of the thirty-three sampling sites selected overseas, and from all eleven sampling sites selected in the United States. One site in the U.S. provided samples of two different grades of MGO raising the total number of samples obtained to forty-two. Permission to obtain samples was not granted in Mexico or Singapore. Although permission to obtain samples was granted in India, government approval to export the samples was not received within the time constraints of the survey.

Sample Handling

Distillate fuel samples were received at SwRI in San Antonio, Texas, USA from mid-June, 1996 through early December, 1996. Once received, the MGO samples were separated from the GVDF samples which were analyzed by SwRI for the Army following a protocol specified by the Army. The MGO samples were handled as follows. Three, one-liter sub-samples were drawn from each five-gallon MGO sample. The sub-samples were contained in new, clean one-liter amber glass bottles. One sub-sample was used in fuel lubricity research being conducted by SwRI for the Navy. The second sub-sample was nitrogen-blanketed and placed in refrigerated storage at 4°C at SwRI. Aliquots of fuel needed to perform the hydrogen content and aromatics content analyses, which were conducted at SwRI, were drawn from this sub-sample. The third sub-sample was nitrogen-blanketed and shipped to NRL for fuel storage stability testing and use in other ongoing research. The balance of the 5-gallon sample was nitrogen-blanketed in the original drum and placed in refrigerated storage at 4°C at SwRI until five samples were accumulated. They were then shipped to USX Engineers and Consultants (UEC), Pittsburgh, PA, USA under contract to the Navy for fuel analysis testing.

The one exception to the above sample handling protocol was the four-liter sample obtained from Kenya. Since the sample size was limited, this fuel was not included in the fuel lubricity research underway at SwRI. One of the four, one-liter bottles of MGO was retained in refrigerated storage at SwRI and was sampled and analyzed for hydrogen content and aromatics content. The second one-liter bottle was shipped to NRL and the remaining two, one-liter bottles were shipped to UEC.

Fuel Property Analyses

The MGO fuel samples were analyzed using all of the fuel property tests required by Military Specification MIL-F-16884J, Fuel, Naval Distillate (NATO F-76) plus additional tests of fuel aromatics content, net heat of combustion, total water content, and fuel lubricity. The results of the fuel analyses as well as the division of the analyses among SwRI, NRL, and UEC are shown in Table 1. In addition to the four distillation temperatures required by MIL-F-16884J (10% point, 50% point, 90% point and final boiling point), the test results reported for atmospheric distillation also included the initial boiling point, 5% point, 95% point, and all intermediate boiling temperatures at 10% recovery intervals over the boiling range.

The MGO test results from the three analysis sites were assembled by NSWCCD, and the degree to which these fuels could be used aboard Navy ships was assessed by comparing the analytical results with two fuel specifications. The comparison specifications were Military Specification, MIL-F-16884J, Fuel, Naval Distillate(NATO F-76) dated 31 May, 1995, and the Naval Sea Systems Command (NAVSEA) Purchase Description for Marine Gas Oil (MGO PD).

Discussion of Results - Comparison with MIL-F-16884J

Only three of the forty-two samples analyzed passed all requirements of Military Specification MIL-F-16884J. The fuels which passed were obtained from refineries in the Netherlands, Panama, and Northern California. Of the remaining 39 samples, seven failed only one specification requirement (either pour point, distillation residue + loss, or particulate contamination), seven failed two specification requirements (such as pour point, cloud point, ash, color, particulate contamination, or distillation residue + loss) and twenty-five failed three or more specification requirements (such as pour point, cloud point, particulate contamination, color, aniline point, distillation end point, or storage stability). Table 2 shows the number of fuel samples that failed each of the required fuel properties ranked in order of most failures to the least failures.

As can be seen in Table 2, the cold flow properties, pour point and cloud point were two of the most restrictive of the specification requirements. The amount by which the fuels failed these requirements varied from one or two degrees above the allowable maximum to 19 degrees above the allowable maximum. Fifteen of the twenty-two fuels which failed the pour point requirement and nine of the thirteen fuels which failed the cloud point requirement were refined in tropical regions. The remaining seven fuels which failed the pour point requirement and the remaining four fuels which failed the cloud point requirement were refined in temperate regions. All of the fuels from Northwestern Europe (Belgium, England, Netherlands and Sweden) passed both the pour point and cloud point requirements.

Of the eleven fuels refined in the United States, the Hawaiian fuel failed both pour point and cloud point requirements. Three other US refined fuels, (Alaska, Florida and Texas) failed the pour point requirement, but passed the cloud point requirement.

Table 2 also shows that the second most restrictive specification requirement was particulate contamination. Eighteen of the forty-two samples failed the particulate contamination requirement. The particulate contamination results generally followed the overall quality of the fuels. Of the fourteen fuels that failed only one or two specification requirements, only one failed particulate contamination, and that one fuel (England) failed by only one mg/l (11 mg/l vs 10 mg/l maximum). In fact, the particulate contamination requirement was the only MIL-F-16884J requirement that the fuel from England failed. Of the twenty five fuels that failed three or more specification requirements, only seven passed the particulate contamination requirement. Typically, government contracts for F-76 stipulate that the storage tanks be dedicated to F-76 only to limit contamination. Since this survey concentrated on obtaining samples of typical commercial fuels, the particulate contamination results may reflect the general level of cleanliness in the fuel systems sampled.

Although color was the fourth most restrictive fuel property, seven of the ten fuels which failed the color requirement did so because they contained dye. Although undyed fuel was sought at all sampling sites, it was not available at eight locations. Six of these fuels which failed the color requirement were obtained from locations within the United States. One fuel sample, which also failed the color requirement, was from Belgium where dye was added as an export marker. Another sample, from the Netherlands, also contained an export dye marker, but it passed the color requirement.

In addition to the ASTM D 1500 color measurement, all of the fuel samples were analyzed by NRL with the PetroSpec dye analyzer which simultaneously measured both the concentration of red dye in the fuel and the color of the base fuel prior to dye addition. The base color of all seven red dyed fuels was shown to be within the MIL-F-16884J color requirement. The PetroSpec dye analyzer also confirmed that the three other fuels which failed the color requirement did not contain dye. Traces of dye, thought to be present through incidental contamination, were also detected in fifteen other fuel samples all of which passed the color requirement. Since the results of the ASTM D 1500 color test were clearly skewed by the presence of red dye in the fuel samples, some means of overcoming this deficiency must be found if the color requirement in MIL-F-16884J is to continue to be of practical use. The PetroSpec dye analyzer appears to be one possible means of addressing this problem.

Only one fuel (Djibouti) had any trace metal contents (0.62 ppm lead) which exceeded the MIL-F-16884J limits. In fact, measurable amounts of the five trace metals mentioned in MIL-F-16884J (calcium, lead, sodium, potassium and vanadium) were found in only eleven of the total forty-two samples and all but one were within specification limits. The presence of trace metals, especially lead and vanadium, can promote hot corrosion of gas turbine engine vanes and blades.

Comparison With the USN Marine Gas Oil Purchase Description

The MGO PD has thirteen fuel property requirements while MIL-F-16884J has twenty six. In addition to having half as many requirements as MIL-F-16884J, the limits specified in the MGO PD for ash content, carbon residue, viscosity and copper corrosion are less restrictive. Table 2 shows the fuel properties covered by both MIL-F-16884J and the MGO PD, and the property limits called for in each.

Fourteen of the forty-two samples analyzed passed all requirements of the MGO PD. The fuels which passed included the three mentioned above as passing MIL-F-16884J (Netherlands, Panama, and Northern California) plus eleven other fuels from refineries in Egypt, England, Djibouti, Kuwait, New Zealand, Senegal, South Korea, Sweden, Venezuela, Alaska, and Texas. This represents one-third of the total number of samples analyzed Of the remaining 28 samples, fifteen failed only one purchase description (PD) requirement (such as cloud point, cetane number/index, carbon residue on 10% bottoms, and color), ten failed two PD requirements (such as cloud point, cetane number/index, flash point, viscosity @ 40°C, and distillation 90% point) and three failed three or more PD requirements.

The three samples which passed all requirements of MIL-F-16884J also passed all of the requirements of the MGO PD. These three fuels would be considered fully compatible with Navy shipboard fuel combustion and fuel handling equipment.

The other eleven fuels mentioned above as passing all requirements of the MGO PD contain properties which did not meet MIL-F-16884J requirements and were not addressed by the MGO PD. For eight of these eleven fuels (England, Kuwait, New Zealand, South Korea, Sweden, Venezuela, Alaska, and Texas), the property deficiencies relative to MIL-F-16884J involved only one or two properties (such as acid number, distillation residue + loss, pour point, and particulate contamination). The Navy's policy of immediately using MGO taken aboard (i.e. within 6 weeks) would probably be sufficient to avoid operational problems with these fuels as long as ship operations were confined to relatively warm waters.

However, for the remaining three fuels (Egypt, Djibouti, and Senegal), the property deficiencies relative to MIL-F-16884J were both more numerous and were sufficiently severe that their use may adversely affect ship operations. These three fuels were all refined in tropical regions and their pour points were up to 19°C above the MIL-F-16884J pour point limit. High pour points can cause filter/injector plugging or pumpability problems. In addition to pour point, the ash content of two of the samples (Egypt and Djibouti) was well above the limit of MIL-F-16884J. A high ash content impacts rates of wear in diesel engines and erosion of gas turbine engine vanes and blades and if used over a significant period of time can lead to premature maintenance.

The storage stability result for one fuel (Djibouti) which passed all MGO PD requirements indicated a potential to form significant amounts of sediment and/or sludge in the shipboard fuel system. There is no fuel storage stability requirement in the MGO PD and as shown in Table 1, there were six samples that failed the storage stability requirement of MIL-F-16884J. Such deposits have the potential to plug filters and/or fuel injectors and can begin to do so as soon as the fuel is brought aboard. Such problems have occurred infrequently both aboard ship and in fuel storage facilities ashore with fuels which at the time of procurement met all requirements of the MGO PD. The most recent such problem was experienced by a U. S. Coast Guard cutter operating off the U.S. East Coast in March/April, 1997. The cutter experienced severe fuel incompatibility/instability problems while operating with fuel meeting the requirements of the MGO PD. The cutter had taken the MGO PD fuel aboard because the fuels above it in the normal order of preference, NATO F-76, NATO F-44 (JP-5), and NATO F-75 (low cloud/pour point F-76), were not available in the area of operation. Although fuel incompatibility/instability was a factor in the operational difficulties experienced, the full cause is still under investigation by the Coast Guard.

CONCLUSIONS

It can be concluded that in general, commercial distillate marine fuels are not satisfactory for continuous use in U.S.N. ships. About one-third of the fuel samples collected were acceptable according to the MGO PD. However, about one-fifth of these fuels (i.e. about seven percent of the total) which are acceptable to the MGO PD also have the potential to cause operational problems because of combinations of off-spec properties such as storage stability, cold flow, carbon residue and particulate contamination. Although short-term and immediate use of the fuels aboard ship may minimize these problems, some increase in fuel-related maintenance can be expected.

While the 1996 Worldwide Survey provided an excellent snapshot of the properties of current commercial distillate marine fuels, it did not address future potential changes in fuel properties, the elements that can drive these changes, nor the impacts these future changes may have on shipboard combustion and fuel handling equipment. Therefore an assessment of the potential changes in the properties of commercial distillate marine fuels over the next ten to twelve years is required to redefine the Navy's shipboard mobility fuels program. Such a redefinition will assure that current specifications will continue to provide adequate protection of the shipboard combustion and fuel handling equipment as well as provide sufficient lead time for potential revision of specifications and/or development of new commercial and/or military specifications to meet the projected fuel property changes in the global fuels marketplace.

Table 1 - Fuel Analysis Results

Property Name Analysis Site ASTM Method Country \ Units	Acid No UEC D 974 mgKOH/g	Aniline UEC D 611 °C	Appear. UEC D 4176	Mono Aromatic SwRI D 5186 wt%	Poly Aromatic SwRI D 5186 wt%	Total Aromatic SwRI D 5186 wt%	Ash UEC D 482 wt%	Carb. Res. 10% Btms UEC D 524 wt%
Belgium	0.06	66.0	C&B	25.30	8.50	33.80	0.009	0.08
Brazil	0.30	72.0	C&B	20.70	9.00	29.70	<0.001	0.22
Canada	0.04	59.0	C&B	21.20	18.40	39.60	0.001	0.16
Chile	0.06	67.9	C&B	17.40	11.50	28.90	<0.001	0.11
Columbia	0.77	72.4	C&B	15.40	8.10	23.50	<0.001	0.14
Egypt	0.06	50.0	C&B	16.40	9.90	26.30	0.009	0.09
England	0.04	65.0	C&B	22.40	11.40	33.80	<0.001	0.04
Djibouti	0.05	65.0	C&B	24.80	12.50	37.30	0.010	0.08
France	0.15	67.0	C&B	19.70	6.00	25.70	0.013	0.07
Greece	0.07	59.3	C&B	26.50	17.80	44.30	<0.001	0.16
Italy	0.05	59.0	C&B	30.90	11.60	42.50	<0.001	0.14
Japan	0.15	65.3	Cloudy	24.10	13.10	37.20	<0.001	0.37
Kenya (1)	0.01	77.3	C&B	17.20	10.70	27.80	<0.001	0.11
Kuwait	0.03	74.0	C&B	22.70	6.50	29.20	0.002	0.11
New Zealand	0.15	69.0	C&B	17.20	9.30	26.50	<0.001	0.07
Netherlands	0.05	68.0	C&B	24.30	8.10	32.40	<0.001	0.10
Okinawa	0.32	71.0	C&B	16.80	8.00	24.80	<0.001	0.11
Pakistan	0.04	69.9	C&B	19.00	9.70	28.70	<0.001	0.02
Panama	0.10	62.5	C&B	17.00	7.30	24.30	<0.001	0.11
Saudi Arabia	0.02	57.5	C&B	30.84	16.39	47.23	<0.001	0.36
Senegal	0.07	68.0	C&B	17.10	9.60	26.70	0.001	0.10
South Africa	0.04	68.8	C&B	19.40	12.60	32.00	<0.001	0.08
South Korea	0.13	79.1	C&B	18.80	7.80	26.60	<0.001	0.06
Spain	0.12	61.0	C&B	22.30	15.70	38.00	0.003	0.18
Sri Lanka	0.04	70.4	C&B	21.18	9.33	30.51	<0.001	0.10
Sweden	0.14	72.0	C&B	15.70	6.50	22.20	<0.001	0.06
Thailand	0.10	78.0	C&B	15.90	8.60	24.50	0.001	0.05
Turkey	0.04	68.2	C&B	20.20	9.20	29.40	<0.001	0.13
UAE	0.03	79.0	C&B	14.30	7.60	21.90	<0.001	0.06
Venezuela	0.11	68.9	C&B	19.20	9.40	28.60	<0.001	0.11
Alaska	0.09	63.0	C&B	19.50	10.10	29.60	<0.001	0.07
California (S)	0.01	63.0	C&B	26.00	4.50	30.50	<0.001	0.10
California (N)	0.02	78.4	C&B	8.30	1.30	9.60	0.002	0.02
Florida	0.17	57.0	C&B	23.90	13.40	37.30	0.008	0.16
Hawaii	0.15	68.0	C&B	17.60	12.10	29.70	<0.001	0.13
Louisiana	0.18	60.1	C&B	21.00	11.20	32.20	<0.001	0.43
New Jersey	0.18	56.0	C&B	25.70	14.20	39.90	<0.001	0.07
South Carolina	0.06	61.2	C&B	22.20	10.60	32.80	0.004	<0.01
Texas	0.32	65.6	C&B	21.60	8.30	29.90	<0.001	0.14
Virginia (A)	0.04	60.0	C&B	21.70	5.50	27.20	<0.001	0.11
Virginia (B)	0.16	47.0	C&B	26.60	16.30	42.90	0.004	0.24
Washington	0.10	61.8	C&B	20.90	9.70	30.60	<0.001	0.06

(1) Sample analyzed by SwRI using Ground Vehicle Diesel Fuel protocol

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Cetane Number UEC D 613	Cetane Index UEC D 976	Cloud Pt. UEC D 2500 °C	Color UEC D 1500	PetroSpec Red dye Analyzer (2) NRL Red Dye ppm	PetroSpec Red dye Analyzer (2) NRL Base Fuel Color	Copper Corros. UEC D 130
Belgium	48.1	50.1	-16.0	6.0	3.5	0.7	1A
Brazil	49.0	49.3	9.0	2.0	0.0	2.4	1A
Canada	43.3	42.6	-18.0	2.0	0.0	2.7	1A
Chile	49.5	48.9	3.0	< 1.5	0.0	1.4	1A
Columbia	50.0	49.5	4.0	< 3.5	0.0	2.5	1A
Egypt	56.6	52.4	-6.0	< 1.5	0.1	1.1	1A
England	49.2	47.3	-18.0	< 1.5	0.0	1.4	1A
Djibouti	50.5	54.8	-15.0	< 2.5	0.0	2.4	1A
France	46.6	49.0	-8.0	< 0.5	0.1	0.2	1A
Greece	41.8	45.8	6.0	2.0	0.0	2.6	1A
Italy	41.7	45.3	-3.0	1.0	0.1	1.0	1A
Japan	46.6	45.9	Too Dark	< 6.5	Too Dark	6.5	1A
Kenya	61.0	52.3	8.2	1.5			1A
Kuwait	53.2	55.3	-16.0	< 1.0	0.0	0.8	1A
New Zealand	50.6	48.9	-17.0	< 0.5	0.3	0.2	1A
Netherlands	50.4	48.9	-25.0	1.0	0.2	0.9	1A
Okinawa	50.2	49.2	3.0	< 1.0	0.1	0.4	1A
Pakistan	56.4	52.9	7.0	< 1.5	0.0	1.0	1A
Panama	44.9	47.7	-12.0	< 1.5	0.0	1.2	1A
Saudi Arabia	42.3	44.3	-1.0	< 1.5	0.3	1.4	1A
Senegal	47.4	47.5	-10.0	< 1.5	0.0	1.1	1A
South Africa	51.7	49.6	1.0	< 1.0	0.2	0.7	1A
South Korea	50.6	51.2	-12.0	< 1.0	0.2	0.5	1A
Spain	45.8	44.9	Too Dark	3.5	0.0	4.2	1A
Sri Lanka	54.2	52.9	4.0	< 1.5	0.0	1.3	1A
Sweden	54.7	53.7	-13.0	< 0.5	0.1	0.2	1A
Thailand	61.8	58.1	17.0	< 0.5	0.3	0.2	1A
Turkey	50.4	50.4	3.0	< 1.0	1.0	0.8	1A
UAE	60.7	59.8	12.0	< 1.0	0.0	0.5	1A
Venezuela	46.0	55.3	-6.0	< 2.0	0.0	1.3	1A
Alaska	46.5	47.2	-15.0	< 0.5	0.0	0.1	1A
California (S)	42.2	45.5	-20.0	< 6.0	19.4	0.3	1A
California (N)	54.5	56.4	-12.0	< 0.5	0.0	0.1	1A
Florida	40.9	41.1	Too Dark	5.5	12.1	2.0	1A
Hawaii	50.7	48.3	8.0	< 0.5	0.4	0.3	1A
Louisiana	43.6	43.6	Too Dark	5.5	15.2	0.1	1A
New Jersey	39.4	41.3	Too Dark	6.5	19.2	0.0	1A
South Carolina	44.6	46.1	-18	< 6.0	12.3	1.9	1A
Texas	47.0	47.5	-6.0	2.5	1.3	1.7	1A
Virginia (A)	39.8	42.7	-21.0	< 1.0	0.3	0.5	1A
Virginia (B)	46.7	37.0	-18.0	< 1.5	0.5	1.0	1A
Washington	44.4	44.7	-20.0	< 6.0	20.5	0.0	1A

(2) The red dye analyzer simultaneously measures both the concentration of dye in the fuel and the color of the base fuel prior to dye addition

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Demuls. UEC D 1401 ml-ml-ml-Min	Density @ 15.6°C UEC D 1298 Kg/M^3	Density @ 15.6°C UEC D 1298 °API	Dist. IBP UEC D 86 °C	Dist. 5% Pt. UEC D 86 °C	Dist. 10% Pt. UEC D 86 °C	Dist. 20% Pt. UEC D 86 °C
Belgium	42-38-0-5	841.8	36.6	170	201	218	223
Brazil	43-37-0-5	859.1	33.2	202	223	234	252
Canada	42-38-0-5	870.2	31.1	182	219	233	248
Chile	42-38-0-5	851.4	34.7	164	188	211	241
Columbia	40-24-16-60	855.5	33.9	192	221	237	253
Egypt	42-38-0-5	847.8	35.4	174	184	231	252
England	42-38-0-5	855.5	33.9	170	187	217	236
Djibouti	40-40-0-5	856.0	33.8	194	209	224	244
France	41-39-0-5	835.8	37.8	162	185	192	208
Greece	42-38-0-5	868.1	31.5	208	229	241	257
Italy	42-38-0-5	854.5	34.1	167	191	204	224
Japan	42-36-2-10	868.6	31.4	173	198	218	249
Kenya	40-40-0-10	852.5	34.5	225		271	
Kuwait	40-40-0-5	850.9	34.8	220	246	254	266
New Zealand	41-39-0-5	858.6	33.3	198	229	241	253
Netherlands	42-38-0-5	856.5	33.7	175	208	221	249
Okinawa	40-40-0-5	860.7	32.9	206	216	235	261
Pakistan	42-38-0-5	840.3	36.9	176	196	208	237
Panama	41-39-0-5	825.3	37.9	186	189	201	211
Saudi Arabia	40-40-0-5	869.7	31.2	197	217	227	244
Senegal	40-40-0-6	866.5	31.8	192	230	244	259
South Africa	42-38-0-5	858.6	33.3	194	220	233	255
South Korea	40-40-0-5	841.8	36.6	168	188	200	223
Spain	42-38-0-5	868.6	31.4	221	226	240	245
Sri Lanka	40-38-0-5	846.8	35.6	192	219	232	251
Sweden	40-40-0-5	838.3	37.3	199	214	221	234
Thailand	42-38-0-5	835.8	37.8	170	223	237	254
Turkey	40-40-0-5	842.3	36.5	172	192	203	227
UAE	42-38-0-5	838.3	37.3	200	230	243	261
Venezuela	45-35-0-5	858.6	33.3	200	225	236	251
Alaska	40-40-0-5	859.7	33.1	196	231	247	262
California (S)	40-40-0-5	858.6	33.3	202	220	229	240
California (N)	40-40-0-5	845.8	35.8	174	202	237	266
Florida	43-37-0-5	852.9	34.4	174	187	200	214
Hawaii	40-40-0-5	866.0	31.9	213	239	252	266
Louisiana	40-40-0-5	860.2	33.0	183	208	221	236
New Jersey	42-38-0-5	865.4	32.0	152	201	216	229
South Carolina	41-36-3-5	854.5	34.1	175	203	216	234
Texas	42-38-0-5	860.7	32.9	199	223	240	252
Virginia (A)	40-40-0-5	845.8	35.8	179	194	209	214
Virginia (B)	40-40-0-5	869.7	31.2	157	179	208	217
Washington	40-40-0-5	858.6	33.3	177	197	210	229

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Dist. 30% Pt. UEC D 86 °C	Dist. 40% Pt. UEC D 86 °C	Dist. 50% Pt. UEC D 86 °C	Dist. 60% Pt. UEC D 86 °C	Dist. 70% Pt. UEC D 86 °C	Dist. 80% Pt. UEC D 86 °C	Dist. 90% Pt. UEC D 86 °C	Dist. 95% Pt. UEC D 86 °C
Brazil	266	279	292	308	327	349	381	406
Canada	258	268	277	286	297	311	331	348
Belgium	239	253	268	279	298	319	343	358
Chile	258	271	282	293	304	317	333	353
Columbia	265	276	287	299	313	332	343	357
Egypt	265	276	287	298	312	329	353	372
England	254	269	282	293	308	323	342	360
Djibouti	260	274	288	299	314	325	346	357
France	225	243	258	272	285	300	322	342
Greece	268	278	288	298	311	326	347	363
Italy	242	257	270	284	300	319	346	374
Japan	274	294	311	327	344	362	389	412
Kenya			310				366	382
Kuwait	276	287	297	308	320	334	355	375
New Zealand	266	276	285	296	308	322	341	357
Netherlands	269	283	294	306	318	324	352	356
Okinawa	276	288	299	310	322	337	352	369
Pakistan	255	268	281	296	307	325	352	381
Panama	223	235	247	260	274	290	313	336
Saudi Arabia	262	278	292	304	318	333	353	371
Senegal	271	282	292	303	316	332	357	377
South Africa	272	284	297	309	322	336	354	368
South Korea	243	264	281	295	311	327	357	373
Spain	256	267	280	292	308	324	346	362
Sri Lanka	263	275	286	290	313	332	361	380
Sweden	249	263	276	289	303	319	344	356
Thailand	265	276	286	298	312	329	351	369
Turkey	244	260	276	289	306	322	348	368
UAE	276	288	299	311	324	338	359	377
Venezuela	264	277	288	300	312	324	342	357
Alaska	272	278	284	289	293	299	306	312
California (S)	251	260	270	281	293	307	328	357
California (N)	279	293	303	311	321	334	345	361
Florida	226	238	248	263	277	294	319	334
Hawaii	276	284	292	299	309	320	336	354
Louisiana	246	257	268	279	291	303	322	339
New Jersey	243	254	264	276	287	302	328	342
South Carolina	249	262	273	284	296	309	329	349
Texas	265	276	286	296	307	320	340	358
Virginia (A)	222	231	241	251	263	277	296	311
Virginia (B)	230	241	251	261	274	288	308	326
Washington	247	263	277	290	303	316	334	352

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Dist. End Pt. UEC D 86 °C	Dist. Residue UEC D 86 vol%	Dist. Loss UEC D 86 vol%	Net Heat of Comb. UEC D 2382 MJ/Kg	Hydrogen Content SwRI D 4808 wt%	Flash Pt. UEC D 93 °C	Partics. NRL D 5452 (3) mg/L
Belgium	370	1.0	0.0	42.752	12.90	66.0	4.2
Brazil	409	1.1	1.5	42.507	13.11	74.4	17.6
Canada	364	1.0	0.5	42.086	12.51	71.0	133.8
Chile	367	1.0	2.0	42.512	13.19	63.3	10.9
Columbia	377	1.0	1.0	42.575	13.40	81.1	20.9
Egypt	387	1.0	1.3	42.619	13.43	76.0	65.6
England	374	1.0	0.0	42.563	12.85	75.6	11.1
Djibouti	377	1.0	0.0	42.435	12.55	75.6	31.1
France	361	1.8	0.2	42.847	13.45	54.0	3.4
Greece	378	1.1	1.0	42.033	12.45	81.0	17.4
Italy	395	1.3	1.1	42.442	12.80	65.6	2.0
Japan	413	1.5	1.3	42.948	12.65	65.6	71.6
Kenya	393	1.6		42.700	13.07	88.0	
Kuwait	384	1.8	1.3	42.773	13.41	97.8	4.0
New Zealand	361	1.6	1.7	42.942	13.29	91.1	0.9
Netherlands	377	1.0	0.0	42.603	13.23	68.0	5.1
Okinawa	374	1.0	1.0	42.586	13.26	83.3	8.1
Pakistan	391	1.2	1.3	42.537	13.31	54.0	4.2
Panama	359	1.0	1.3	42.644	13.48	71.0	10.0
Saudi Arabia	382	1.3	1.2	42.154	13.03	86.0	2.1
Senegal	383	1.4	2.0	42.828	13.03	81.0	11.5
South Africa	383	1.3	0.6	42.509	12.92	80.0	23.3
South Korea	385	1.0	1.0	42.852	13.33	64.4	3.4
Spain	379	1.0	0.3	42.214	12.64	75.6	64.9
Sri Lanka	383	1.1	4.4	42.412	13.33	79.0	18.6
Sweden	362	1.4	2.2	43.130	13.60	84.0	0.9
Thailand	372	1.2	0.7	42.691	14.11	71.1	3.6
Turkey	378	1.0	1.0	42.465	13.43	68.0	16.7
UAE	387	1.5	1.2	42.826	13.72	81.1	6.0
Venezuela	362	1.4	1.7	42.493	13.11	79.0	9.9
Alaska	323	1.2	0.7	42.437	13.02	74.4	1.6
California (S)	373	1.4	1.3	42.063	13.15	76.0	1.5
California (N)	369	1.0	1.0	43.421	13.64	70.0	3.7
Florida	343	1.0	1.0	42.373	12.56	70.0	19.9
Hawaii	370	1.0	1.2	42.430	12.94	87.0	39.4
Louisiana	349	1.0	1.0	42.826	12.86	74.4	16.1
New Jersey	359	1.8	0.2	42.305	12.29	60.0	4.5
South Carolina	355	1.3	2.0	42.930	12.98	62.2	25.5
Texas	372	1.0	0.0	42.465	13.16	104.4	2.1
Virginia (A)	335	1.0	1.0	42.647	13.47	69.0	7.3
Virginia (B)	338	1.2	0.3	42.005	12.38	67.8	1.2
Washington	356	1.2	2.0	42.502	12.89	65.6	4.2

(3) Test method modified per MIL-F-16884J - total fuel filtered = one liter

Table 1 - Fuel Analysis Results (cont'd)

				TRACE METALS (4)				
Property Name Analysis Site ASTM Method Country \ Units	Pour Pt. UEC D 97 °C	Storage Stability NRL D 5304 mg/100ml	Sulfur UEC D 4294 wt%	Ca UEC ICP/AES ppm wt.	Pb UEC ICP/AES ppm wt.	K UEC ICP/AES ppm wt.	Na UEC ICP/AES ppm wt.	V UEC ICP/AES ppm wt.
Belgium	-18.0	0.7	0.18	<0.1	<0.1	<0.1	<0.1	<0.1
Brazil	-1.0	0.6	0.56	<0.1	<0.1	<0.1	<0.1	<0.1
Canada	-5.0	12.4	0.44	<0.1	<0.1	<0.1	<0.1	<0.1
Chile	0.0	0.5	0.17	<0.1	<0.1	<0.1	<0.1	<0.1
Columbia	-5.0	0.5	0.43	0.61	<0.1	<0.1	0.10	<0.1
Egypt	13.0	0.6	0.33	<0.1	<0.1	<0.1	<0.1	<0.1
England	-15.0	0.7	0.08	<0.1	<0.1	<0.1	<0.1	<0.1
Djibouti	-5.0	1.7	0.72	<0.1	0.62	<0.1	<0.1	<0.1
France	-18.0	0.2	0.20	<0.1	<0.1	<0.1	<0.1	<0.1
Greece	-6.0	0.9	0.55	<0.1	<0.1	<0.1	<0.1	<0.1
Italy	-16.0	0.3	0.19	<0.1	<0.1	<0.1	<0.1	<0.1
Japan	-1.0	2.2	0.98	<0.1	<0.1	<0.1	<0.1	<0.1
Kenya	6.0	0.9	0.64	<0.05	<0.05	<0.01	<0.01	0.16
Kuwait	4.0	0.5	0.42	<0.1	<0.1	<0.1	0.10	<0.1
New Zealand	-7.0	0.3	0.24	<0.1	<0.1	<0.1	<0.1	<0.1
Netherlands	-13.0	0.3	0.18	<0.1	<0.1	<0.1	<0.1	<0.1
Okinawa	-10.0	0.0	0.36	<0.1	<0.1	<0.1	<0.1	<0.1
Pakistan	-2.0	0.3	0.91	<0.1	<0.1	<0.1	<0.1	<0.1
Panama	-20.0	1.2	0.51	<0.1	<0.1	<0.1	<0.1	<0.1
Saudi Arabia	-4.0	0.2	0.51	<0.1	<0.1	<0.1	<0.1	<0.1
Senegal	5.0	0.6	0.13	<0.1	<0.1	<0.1	0.10	<0.1
South Africa	0.0	1.1	0.42	<0.1	<0.1	<0.1	<0.1	<0.1
South Korea	0.0	0.5	0.71	<0.1	<0.1	<0.1	<0.1	<0.1
Spain	-10.0	2.6	0.48	<0.1	<0.1	<0.1	<0.1	<0.1
Sri Lanka	-4.0	0.2	0.59	<0.1	<0.1	<0.1	<0.1	<0.1
Sweden	-13.0	0.0	0.09	<0.1	<0.1	<0.1	0.10	<0.1
Thailand	11.0	0.3	0.23	<0.1	<0.1	<0.1	<0.1	<0.1
Turkey	0.0	0.9	0.75	<0.1	<0.1	<0.1	<0.1	<0.1
UAE	2.0	0.1	0.37	<0.1	<0.1	<0.1	<0.1	<0.1
Venezuela	-10.0	0.3	0.50	<0.1	<0.1	<0.1	<0.1	<0.1
Alaska	-1.0	0.6	0.46	<0.1	<0.1	<0.1	<0.1	<0.1
California (S)	-10.0	0.8	0.01	<0.1	<0.1	<0.1	0.10	<0.1
California (N)	-10.0	0.1	0.01	<0.1	<0.1	<0.1	<0.1	<0.1
Florida	-2.0	2.3	0.34	<0.1	<0.1	<0.1	0.15	<0.1
Hawaii	0.0	0.4	0.41	<0.1	<0.1	<0.1	<0.1	<0.1
Louisiana	-20.0	0.4	0.10	<0.1	<0.1	<0.1	<0.1	<0.1
New Jersey	-25.0	0.7	0.10	<0.1	<0.1	<0.1	<0.1	<0.1
South Carolina	-24	2.7	0.05	0.22	<0.1	<0.1	<0.1	<0.1
Texas	-5.0	0.3	0.43	<0.1	<0.1	<0.1	<0.1	<0.1
Virginia (A)	-25.0	1.0	0.04	<0.1	<0.1	<0.1	<0.1	<0.1
Virginia (B)	-25.0	1.4	0.16	<0.1	<0.1	<0.1	<0.1	<0.1
Washington	-15.0	0.5	0.42	<0.1	<0.1	<0.1	0.10	<0.1

(4) Trace metals were measured using the Inductively Coupled Plasma - Emission Spectrometer Method

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Viscosity @ 40°C UEC D 443 mm^2/sec	Total Water UEC D 1744 ppm	Water & Sediment UEC D 2709 vol%	Lubricity HFRR (5) SwRI D 6079 mm	Lubricity BOCLE (6) SwRI D 5001 mm	Lubricity SLBOCLE (7) SwRI D 6078 grams
Belgium	2.783	182	<0.005	0.295	0.570	5550
Brazil	4.605	261	<0.005	0.165	0.570	7000
Canada	3.243	158	<0.005	0.195	0.570	6100
Chile	3.206	139	<0.005	0.215	0.550	4050
Columbia	4.190	226	<0.005	0.170	0.580	6150
Egypt	3.939	132	<0.005	0.250	0.560	4850
England	3.083	176	<0.005	0.285	0.580	5050
Djibouti	3.483	176	<0.005	0.345	0.600	5200
France	2.432	108	<0.005	0.215	0.580	4300
Greece	3.665	137	<0.005	0.300	0.550	5600
Italy	2.888	212	<0.005	0.435	0.630	4500
Japan	4.522	282	<0.005	0.175	0.590	7000
Kenya	5.000	157		0.205	0.580	5150
Kuwait	4.245	207	<0.005	0.220	0.580	6150
New Zealand	3.844	179	<0.005	0.155	0.550	4600
Netherlands	3.847	163	<0.005	0.335	0.580	3950
Okinawa	4.545	147	<0.005	0.150	0.590	6150
Pakistan	3.206	90	<0.005	0.305	0.620	6000
Panama	2.411	392	<0.005	0.220	0.560	4300
Saudi Arabia	3.555	71	<0.005	0.330	0.610	4950
Senegal	4.449	220	<0.005	0.170	0.520	5500
South Africa	4.073	61	<0.005	0.285	0.570	5150
South Korea	3.078	221	<0.005	0.250	0.600	5600
Spain	3.557	181	<0.005	0.180	0.590	5350
Sri Lanka	3.667	113	<0.005	0.275	0.590	5000
Sweden	3.104	283	<0.005	0.265	0.520	4900
Thailand	3.701	276	<0.005	0.175	0.540	5800
Turkey	2.979	159	<0.005	0.250	0.610	4800
UAE	4.240	350	<0.005	0.320	0.580	6900
Venezuela	4.034	142	<0.005	0.200	0.570	5500
Alaska	3.584	337	<0.005	0.165	0.570	6150
California (S)	3.229	200	<0.005	0.375	0.600	4350
California (N)	4.074	388	<0.005	0.405	0.630	2600
Florida	2.313	199	<0.005	0.220	0.580	5050
Hawaii	4.332	150	<0.005	0.225	0.560	5550
Louisiana	2.845	194	<0.005	0.245	0.540	6350
New Jersey	2.783	156	<0.005	0.250	0.580	4650
South Carolina	2.865	214	<0.005	0.325	0.590	4600
Texas	3.816	138	<0.005	0.180	0.580	4800
Virginia (A)	2.268	153	<0.005	0.400	0.600	3800
Virginia (B)	2.312	169	<0.005	0.340	0.590	3450
Washington	3.057	225	<0.005	0.165	0.550	5950

(5) High Frequency Reciprocating Rig

(6) Ball-On-Cylinder Lubricity Evaluator

(7) Scuffing Load Ball-On-Cylinder Lubricity Evaluator

Table 2 - Failure Ranking of MGO Properties Relative to MIL-F-16884J and MGO PD

	MIL-F-16884J		MGO PD	
Property	Limits	Failures	Limits	Failures
Pour Point, °C	-6 (max)	22		
Particulate Contam., mg/L	10 (max)	18		
Cloud Point, °C	-1 (max)	13	-1.1 (max)	13
Color	3 (max)	10	3 (max)	10
Aniline Point, °C	60 (min)	8		
Distill. Residue + Loss, vol.%	3.0 (max)	8		
Distillation End Point, °C	385 (max)	7		
Storage Stability, mg/100 ml	1.5 (max)	6		
Viscosity @ 40°C, mm^2/sec.	1.7 - 4.3	6	1.7 - 4.5	4
Ash, wt.%	0.005 (max)	5	0.01 (max)	1
Carbon Residue on 10% Btms, wt%	0.20 (max)	5	0.35 (max)	3
Ignition Quality				
Cetane No.	42 (min)	5	42 (min)	5
Cetane Index	43 (min)	5	43 (min)	5
Distillation 90% Point, °C	357 (max)	3	357 (max)	3
Acid Number, mg KOH/100ml	0.30 (max)	3		
Hydrogen Content, wt.%	12.5 (min)	3		
Demulsification, minutes	10 (max)	2		
Flash Point, °C	60 (min)	2	60 (min)	2
Appearance (1)	C&B	0	C&B	0
Copper Corrosion	1 (max)	0	3 (max)	0
Density @ 15.6°C, Kg/M^3	876(max)	0	876(max)	0
Sulfur Content, wt.%	1.0 (max)	0	1.0 (max)	0
Trace Metals				
V ppm	0.5 (max)	0		
Na + K ppm	1.0 (max)	0		
Ca ppm	1.0 (max)	0		
Pb ppm	0.5 (max)	1		
Water and Sediment, vol.%	0.05 (max)	0	0.05 (max)	0

(1) Fuels were considered to pass the appearance requirement with a rating other than "Clear and Bright" if they met both the Water and Sediment requirement of 0.05 vol.% (max) and the Particulate Contamination requirement of 10 mg/L (max)