Stable mixtures of distillate fuels and water

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SYNOPSIS The development of additives to treat diesel fuels contaminated with water is described. Consideration is given to the need to ensure compatibility with metallic and non-metallic materials with which treated fuels are in contact to avoid the risk of breakdown of otherwise stable mixtures. This stability is essential to avoid problems of poor engine performance, corrosion of system components and the accumulation of unwelcome deposits. A discussion is also included of experiments to produce stable mixtures containing ethanol and renewable fuel oils derived from animal and vegetable sources.

1   INTRODUCTION

There has been an interest over many years in creating mixtures of water and higher distillate fuels for use in internal combustion engines. The principal reasons are to achieve increased power output and potential improvements in exhaust emissions.

A fundamental problem that most researchers and plant operators have encountered has been the stability of the resultant fuel-water mixture. Fairly rapid separation of the fuel and water has led to problems of poor running, corrosion of system components in the fuel train (from fuel tank to engine), often aggravated by the development of bacteria and fungal growth.

The usual intention appears to have been the addition of significant quantities of water. In a series of tests commissioned at City University some 5-6 years ago by various merchant banks to assess the merits of three proposed fuel additives the intended water addition to the fuel was in the region of 15—30 percent. This may be contrasted with the efforts made by fuel companies to eliminate water from their products and the need to include filters and water traps to overcome the well-known problems described above.

Against this background a research programme was initiated at City University to develop a method for treating water contaminated diesel fuel oils. Whilst in the long term the intentional addition of water could be a desirable goal, it was felt that the formulation of an additive that would overcome problems associated with water contamination was a sufficiently important goal in itself. Subsequent interest by plant operators, commercial and pleasure sections of the marine industries etc., has confirmed the validity of this approach.

2   DEVELOPMENT STRATEGY

Among the self—imposed constraints were the requirements that not only would a resultant fuel additive satisfactorily combine modest quantities of water with a fuel but it would not require any modifications to engines or associated equipment and it would be acceptable to engine manufacturers in that it would not invalidate their warranties. Other, perhaps obvious, constraints were that additives should not contain or produce toxic or otherwise harmful substances and require no more special care in •their use than common

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domestic cleaners and similar substances.

It was apparent at a very early stage that the key issue to finding a satisfactory solution(!) to the problem was the stability of the resulting mixtures. From literature as well as discussions with interested parties other research programmes appeared to have foundered on this difficulty. Insofar as some successes with water addition had been achieved they had required that fuel systems be flushed through adequately with neat fuel before shutting engines down, or had required modifications to allow direct water injection near the engine.

In principle the process of formulating an additive could be approached theoretically. This would require, however, an immense level of knowledge about potential additive ingredients, mainly from the wide range of surfactants available. This knowledge is really not there, and so the process becomes something of a "black art" requiring an element of "chemical common sense", intuition and luck.

Using an iterative experimental approach a first generation additive mixture was formulated comprising six ingredients. These formed a bridge between surfactants that, individually, were miscible in water anddiesel oil at the extreme but were then miscible in intermediate but compatible fluids. These six ingredients became the chemical building blocks that have individually been the subject of further recent research, to be discussed later.

Although contamination by 1-2 percent water- in oils was the initial target, in the interests of experimental accuracy in determining the optimum relative proportions of the ingredients, water: fuel mixtures in the ratio 1:10 were used during the early development.

Many formulations were tried but although emulations were created that ran satisfactorily in a Ricardo E—6 fuel research engine, they invariably broke phase within days, if not hours. Nevertheless a formulation was ultimately achieved which gave a good stable result. The treated fuel remained stable for days, which stretched into weeks and ultimately months and now, several years.

Meanwhile, having achieved at least a prima facie success, we moved on to the materials and compatibility testing.

3 STABILITY AND MATERIALS COMPATIBILITY

The stability of both the fuel additives and of treated contaminated fuel means more than remaining unchanged in a sealed glass bottle on a laboratory shelf. It has been interpreted as the extent to which they are affected or not by contact with the various materials that one might encounter between the fuel tank and the combustion chamber as well as due to changes in temperature.

A matrix of test samples was set up to test the reactions (if any) of metallic and non-metallic substances on neat fuel, water, fuel-water mixtures with and without the additives, neat additives and with the separate constituent ingredients of the additive,

Materials that have been tested for a reaction include sheet steel as used in fuel tanks, various tubes of steel, copper, reinforced nylon and synthetic rubber (bundy tubing), brass (as in olives and some connectors), aluminium alloys to represent fuel filter and pump cases, and sheet rubber.

In addition to tests in which specimens were completely immersed in the various solutions, a set of tests was conducted for the steel plate in which samples were not completely submerged to simulate partially full fuel tanks. Some samples were set up and left to stand, some were inverted once and then left, and others were inverted daily for a period of 15 weeks to simulate changing levels in fuel tanks due to continuous emptying and refilling. All of the other samples were monitored but in general were left undisturbed.

Of the eight materials tested the only metallic ones to show a visible reaction were the copper and brass. Over a period of some time a bluish haze appeared in the fluid adjacent to the metal surface. Whether this reaction derives purely from creating a surface coating on the specimens or is a progressive attack is at present unresolved. Although there was a small loss in weight it was so small that it is unclear whether it was due to the material being etched away or mechanical removal during the careful drying and cleaning required before weighing the specimens. From a practical point of view, the slight reactions with brass and copper are not regarded as important since there is very little of either of these materials in the fuel system.

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Of much greater significance were the results with both aluminium alloys and steel where there appeared to be no effect whatsoever.

In the case of the simulated fuel tank corrosion tests the results indicated that the use of the additive in diesel—water mixtures enables the water to be sufficiently bonded so as not to affect the steel. Even in tests where insufficient additive was used such that an opaque emulsion was formed, rusting of the steel did not occur.

Although these tests indicated that neither a solution (i.e. micro—emulsion) nor emulsion caused corrosion problems in themselves a subsequent breakdown in a coarse emulsion could ultimately lead to problems as the water phase became increasingly isolated.

With the non—metallic substances there were, with the exception of the natural sheet rubber, no significant differences in the effects produced by the various combinations of water, fuel additive or additive components. Effects did occur — for example the reinforced nylon tube absorbed red dye from the diesel fuel, and over a period of time hardened but the addition of water with or without additive did not alter this. Similarly the bundy tubing increased in weight in all cases — to a greater effect with the treated diesel but not to an extent that is regarded as unacceptable.

It was noted in this series of tests that the treated fuel water mixtures having sufficient additive in them to be clear and transparent have continued to remain so, but the opaque emulsions ultimately broke phase. It was also observed that the rate at which they did so was influenced by the materials with which they were in contact.

4 SECOND AND THIRD GENERATION FORMULATIONS

Associated, and in parallel, with the stability and materials compatibility tests, a programme of component substitution has been pursued. This had the twin aims of improving on the efficiency of the Mark I formulation and of avoiding reliance on either an individual ingredient or manufacturer. Success has been achieved in both these respects.

Improving efficiency is interpreted as requiring less additive to combine a given quantity of water with the fuel oil and to achieve a stable result. In practical terms this means that the treated fuel is transparent, though not necessarily haze free.

The order in which the additive, oil and water are combined is immaterial. The end result is the same though the intermediate stages differ.

When the water is added to the oil first it settles to the bottom of the container. Pouring in the additive and gently stirring yields an opaque mixture which then clears as further additive is mixed In - becoming a transparent though hazy solution. If left for a period of time, half an hour or so, it normally becomes crystal clear and indistinguishable from the neat fuel. The same effect can be achieved without a time delay by mixing in a further small quantity of additive

When the additive is mixed in with the oil first, i.e. before the water, there will be either no visible change or at most a slight hazing. The addition of water leads initially to hazy streaks which then disappear as the water is distributed throughout the total volume.

Taking either the slightly, or crystal clear, "solution" of oil, water and additive as the objective for a stable result it has been possible to reduce the overall total quantity of additive required with the second and third generation versions.

5 TOLERANCE ON FORMULATION

The mechanism by which the water, oil and various components that make up the family of additives combine is difficult to resolve. Mixtures of water:diesel oil in the range 2 : 100 to 15 : 100 have been achieved satisfactorily in terms of the criteria defined above.

However, the proportion of additive required is not related in a simple way to changing proportions of

water to oil. Indeed, even within the additive, the optimum "recipe" for 2 percent contamination is different to that for 10 : 100 or 15 : 100 mixtures. Figure 1 illustrates a typical variation for one generation.

Other observations include the fact that less additive is required when the mixing is in an open topped beaker rather than a bottle with stopper in it, suggesting an interaction with the atmosphere. Also, once the water has been distributed invisibly within the oil, further modest quantities of water can also be absorbed.

6   WATER AS AN ADDITIVE

Although the research programme focussed on the development of an additive to enable water to be combined readily with diesel oils the nature of some of the ingredients that form the additive prompted questions aoout whether variants could   be   produced   for   other "contaminants which might be viewed beneficially. For example; instead of using derivatives of alcohols and vegetable oils to absorb water, could water plus appropriate surfactants be used to combine alcohols or natural oils with diesel oil?

In the case of alcohols ethanol and methanol frequently appear in the literature as substances suggested as an aid to combustion. For assistance in cold starting of diesel engines the addition of alcohol is sometimes recommended as a means of reducing carbon dioxide and hydrocarbon emissions.

Ethanol, being an easily producible alcohol from renewable biological sources, has been examined. It combines readily with pure diesel oil, but even low contamination levels of water cause it to separate out. However, using constituents from the second generation additive for diesel—water mixture, plus water, 20 parts ethanol to 100 parts diesel remained in stable solution for some considerable time.

As with the stability and compatibility tests described earlier a matrix of tests was conducted. Many samples using various proportions of the basic additive components increased the period of stability from a matter of hours to over 123 days, and one case exceeded 218 days.

Interest in the use of animal and vegetable oils as renewable sources of liquid fuels either alone or to prolong the availability cf the traditional capital hydro-carbon sources is Increasing. A major problem with the animal and vegetable oils is the tendency to produce gums and deposits at an unacceptable rate but current developments in the field of genetic engineering should reduce these problems, especially with the vegetable
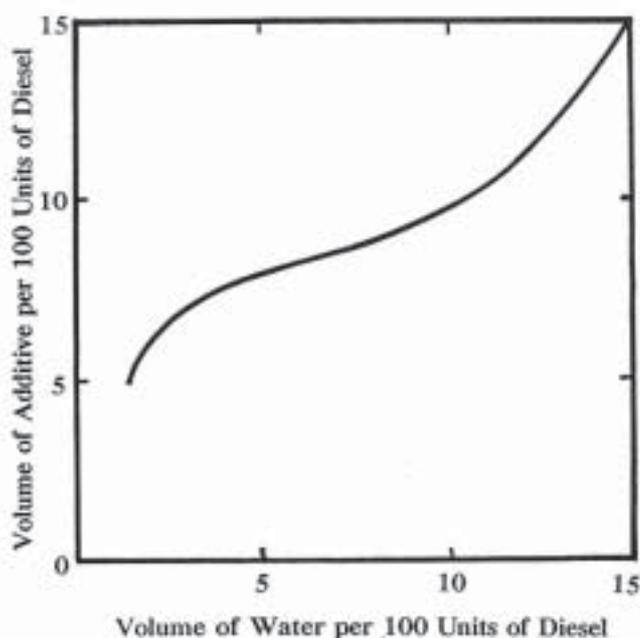

Fig 1   Amount of additive required for various proportions of water to diesel fuel

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oils. Animal fats tend to be more seasonally variable and inconsistent than the vegetable oils.

Again using components from the second generation of diesel-water fuel additive both animal and vegetable oils have been satisfactorily combined with diesel oil. The latter case has been described previously (1) where a modified fuel based on diesel contained approximately 20 percent butter oil. Other, more recent, tests using tallow have been successful, both from the standpoint of creating stable solutions of tallow, diesel and additive, but also in terms of engine performance. Nevertheless it is believed that greater promise exists with the exploitation of vegetable oils both as fuel extenders as well as In their own right.

7   ENGINE TESTS AND FIELD TRIALS

This report has concentrated on the essential, methodical, bench—top aspects of additive development and evaluation. Performance testing in engines has not been overlooked and has been partially reported elsewhere (1). Only a few brief comments are included here for completeness.

At 1-2 percent levels of water contamination changes in engine performance are within the error bands of measurement as one might perhaps expect, though one can say that in the presence of the 1st, 2nd and 3rd generation additives the engines (Ricardo E6 and Ford 2.3 litre 4 cylinder) ran perfectly smoothly.

As the water concentration increases towards 10 percent greater power output can be achieved at low-medium engine speeds. At higher speeds it deteriorates due to the reduction, in the rate of combustion which countinues after the exhaust valves open. This can be partially remedied by advancing the injection timing although this contravenes the requirement to avoid changes to the engine settings.

The first generation, or Mark I, version of the additive to treat contamination by water has been available in the public domain since late 1989. The intention has been to gauge reactions to its use in uncontrolled conditions rather than the more clinical environment of a university research labpratory. The feedback is necessarily anecdotal but apart from being positive serves to confirm the earlier conclusions about tolerance.

Fuel tanks that have been heavily contaminated over a period of time with water can be treated with a sufficiently large addition of additive during a refilling operation. Subsequent very small doses then enable the treated fuel to absorb condensation from tank walls and roof as well as accidental ingress of water from rainfall or other reasons.

8   CONCLUDING REMARKS

A group of chemicals, primarily surfactants, has been identified which, when arranged in a suitable combination, provide an enabling technology to combine water and certain other substances in stable mixtures with diesel fuel oils.

In addition to remaining stable over considerable periods of time, it has also been demonstrated that contact with the usual materials encountered in fuel systems between the fuel tank and combustion chamber will not produce any reactions that mitigate against their use. In particular, no adverse reactions with steels, aluminium alloys and non—metallic substances such as flexible fuel hoses were noted.

Current work is directed towards developing an additive to treat water contaminated petrol in which some success has been achieved. Further work will be related to diesel fuel extenders based on vegetable oils, and problems associated with the heavier fuel oils, lubricating oils and hydraulic fluids.

REFERENCES

(1)   THORLEY A. R. D. and SIMONSON J. R. The development of an additive to treat water contaminated diesel fuel oils. *Petroleum Review,* December 1988, Vol. 42, No. 503, pp 31-34.