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Research Article

Nanoemulsion Fuel Additive Used as a Diesel Combustion Catalyst

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This research article discloses how a uniquely structured fuel additive can easily be mixed with commercially available diesel fuel to produce an extremely stable nanoemulsion fuel. Even when using an ultralow dose (125 ppm), the additive still creates a large and catalytically active surface area using billions of nanosized water droplets (4 nanometers). No metallic or organometallic compounds were used. When used in heavy duty diesel engines, treated fuel significantly improves vehicle fuel economy. Extensive verification testing was carried out using multiple fleets of heavy duty diesel trucks operating for up to two years under "real-world" driving conditions. Testing used 538 heavy duty trucks and 15 different vehicle fleets. Test vehicles used 475,000 litres of treated fuel and covered a total of 14 million kilometres. Fleet testing was supervised by one of the premier European testing agencies (TNO Quality Services BV). Raw fuel economy data was collected and analyzed by an independent consulting agency andd showed a combined average weighted fuel savings of 9.7%. Diesel engine CO_2 emissions are one of the many contributory causes of global warming. Unfortunately, new engine fuel economy technologies can take 10 years to have a 50% impact (typically 5% per year, as older vehicles are slowly replaced with new models). However, using the additive would immediately improve the combustion properties of fuel being used in these vehicles with the potential to reach up to 90% of the entire diesel vehicle population within about 60 days.

1. Introduction

1.1. Motivation. It is generally accepted that reducing the environmental impact of burning fossil fuels is an important goal. One of the ways to help in this area is to address mobile source emissions from on-road and off-road vehicles. Most of the recent advances in reducing vehicle exhaust emissions and/or improving fuel economy have been made in the various areas of engine technology and exhaust after treatment. By comparison, relatively few advances have been made from any improvements to the fuels being used in these vehicles. From an environmental impact point of view, most current fuel additives are aimed at preventing or reducing various engine carbon deposits. Consequently, these additives generally reduce regulated tailpipe emissions such as HC, CO, NO_x, and PM. However, the emission with the highest potential for impacting the environment (global warming and/or climate change) would be CO_2, and this is an area where using emulsion fuels may show the most potential.

It is well known that water can be used to improve the combustion of liquid hydrocarbon fuels, with water normally being introduced into combustion chambers together with fuel in the form of an emulsion of some kind [1]. The earliest patents in this field date back to the 1920s [2]. Unfortunately, emulsion fuels tend to be too expensive and too unstable for practical purposes and have never been widely accepted [3]. For a literature review of emulsion fuels, see reference [4]. However, the benefits from using an emulsion fuel can be significant and this remains an active area for fuel combustion researchers [5, 6]. Nevertheless, emulsion fuels still have the potential to deliver significant benefits not typically provided by conventional fuels [7].

1.2. Existing Fuel Emulsion Technology. A typical fuel emulsion contains a major proportion of oil (or fuel in this case), together with minor amounts of water and a chemical surfactant of some kind. Optionally, a cosurfactant, such as a low molecular weight alcohol, may also be included. More sophisticated fuel emulsions usually contain multiple surfactants [5, 6]. Also, "nanoemulsions" are becoming more popular [8–10].

Macroemulsions of diesel fuel containing 10-micron water droplets have been commercially produced and employed as fuels for heavy duty diesel trucks [3]. However, due to the relatively "large" size of the emulsified water droplets, these fuels tend to have a limited shelf life [11].

Inherently more stable are microemulsions, where the water droplets suspended in the fuel are extremely "small" (typically smaller than the wavelength of visible light or less than about 400 nanometers). This small size renders the fuel emulsion optically clear and also very stable. According to Stokes' Law, the settling rate of water droplets in fuel reduces significantly as the droplet sizes reduce [12]. Therefore, stabilities of microemulsions compared to those of macroemulsions are typically measured in months and years rather than days and weeks [11]. However, the major disadvantage of microemulsion fuels is their complexity and difficulty/cost of production [11].

Microemulsion structures are quite complex, where the physical and chemical properties can vary significantly with changes in the relative proportions of the key ingredients: water, surfactant(s), cosurfactant(s), and oil (or hydrocarbon fuels in this case) [11].

From a purely practical point of view, bulk production of a fully formed microemulsion diesel fuel would present severe logistical problems. Raw diesel is comingled and distributed across the USA by underground pipeline systems and subsequently the brand distinguished by the addition of unique additive packages upon arrival at major fuel distribution terminals. Using a fuel additive that could be easily dosed at these major distribution terminals has the potential to solve this logistical problem.

1.3. Structure of the Article. The Materials and Methods section which follows has been divided into three parts:

(i) *Additive Development.* This gives a brief history of how the additive was developed from existing fuel emulsion technology through four distinct stages into the final development of a nanoemulsion fuel additive.

(ii) *Performance Verification Testing.* This describes the technical problems associated with testing the performance of a nanoemulsion fuel additive and how an extensive field test protocol was developed and implemented in order to statistically verify product claims.

(iii) *Additive Mechanism of Action.* Extensive field performance testing verifies that the additive is very effective in improving heavy duty truck fuel economy under "real life" driving conditions. However, the exact mechanism of action requires substantial academic research well beyond the scope of the additive developers. This section speculates on one of the possible mechanisms of action and is intended as a typical "proof of concept" with the hope that others more qualified to determine the exact mechanism of action will be encouraged to take the matter further.

2. Materials and Methods

2.1. Additive Development. The additive was developed as a concentrate able to produce relatively stable emulsion structures when mixed with diesel fuel. This presented some serious technical challenges since any emulsion is inherently a dynamic system with stability issues depending upon such things as ambient temperature cycles during storage, turbulence while being stored in a vehicle fuel tank, and high shear forces when being injected through an injector spray nozzle [11]:

(i) Emulsion storage stability was achieved by manipulating the relative proportions and quantities of the key ingredients used to produce the additive. Testing for the stability of the additive structure and subsequent emulsion fuel used an informal mixture of trial and error, accidental discoveries, extremely boring iteration, and occasional flashes of intuition followed by repeated cycles of cooking and freezing. Test samples of the additive are still clear and bright even after several years under typical storage conditions.

(ii) Emulsion performance testing of the additive was achieved by measuring fuel economy effects using a small fleet of dedicated drivers and test vehicles driven "over the road" under typical everyday conditions. The classical scientific method was not followed. Instead, simple trial and error iteration was used. Small changes were made to the emulsion structure of the additive, and then road tested in a vehicle to see the resulting effects (if any). After several years, test drivers became extremely sensitive as to how their test vehicles reacted to such changes.

More information regarding the surfactant chemistry and methods used to produce and test the additive can be found in US patent #7,887,604 [13].

In order to be useful and practical, the emulsion structure must be extremely stable under two completely different liquid states:

(i) As a concentrated fuel additive, prior to being mixed with diesel

(ii) After being mixed with diesel, as a fully developed fuel emulsion in storage tanks, vehicle tanks, and engine fuel systems

When sizes are given for emulsified water droplets, these sizes always refer to water droplet diameters in the fuel and not in the additive. Also, when an exact diameter size is quoted for the water droplets, this refers to approximately the midpoint of the size distribution.

The four significant stages of additive development were generally as follows:

(1) Macroemulsion "*whole fuel*," 10 to 15% water content: fuel emulsion with 4 micron water droplets (confirmed using an optical microscope)
(2) Macroemulsion "*additive*," dose ratio 400 : 1: fuel emulsion with 4-micron water droplets (confirmed using an optical microscope)
(3) Microemulsion additive, dose ratio 4,000 : 1: fuel emulsion with smaller than 400 nanometer water droplets (confirmed by emulsion optical clarity)
(4) Nanoemulsion additive, dose ratio 8,000 : 1: fuel emulsion with less than 4 nanometer water droplets (confirmed by using a PSD measurement instrument: Coulter Delsa 440SX) [14]

It is theorized the 4 nanometer water droplets (Stage 4) are approximately spherical and fully enclosed within a surfactant membrane, with the outer shell of this surfactant membrane presenting negatively charged surfactant "tails", giving each emulsified droplet a negative charge [11] (see Figure 1).

Commercial pressure to remain competitive was a motivation for gradual chronological development and was focused on reducing the per liter treat cost by changing the additive dose ratio while improving (or at least maintaining) basic fuel economy performance benefits.

Based on this 4-stage chronology of additive development (each step consecutively reduces both droplet sizes and dose ratio), it was, therefore, speculated that droplet surface area was the critical fuel saving aspect of the fuel emulsion technology:

(i) For emulsion fuel technology Stage 1, emulsified fuel having a 10% water content comprising multiple 4-micron water droplets creates a total droplet surface area of 150 square meters per liter of fuel
(ii) Calculating the same total surface area for Stage 4 with 4-nanometer droplets using a dose ratio of 8,000 : 1 gives an almost identical total surface area of 187.5 square meters

Also critical to the development of the surface area is the droplet size distribution. Most of the additive volume is in the larger droplets, while most of the surface area is in the smaller droplets. Therefore, narrowing the size distribution was also critical to the efficient creation of surface area (see Figure 2).

2.2. Performance Verification Testing. Fuel additive performance claims for heavy duty diesel engines are typically verified by using formal stationary engine dynamometer testing using the FTP (Federal Test Procedure) heavy-duty transient cycle (40 CFR 86.1333). However, this test necessarily requires the fuel additive to have an immediate effect as well as having no residual effect. Unfortunately, informal road testing showed the additive does not have an immediate effect and also displays a significant residual effect. Consequently, this FTP test was not considered appropriate for fuel economy improvement claims verification for this type of fuel additive. The USEPA recognizes a different technique

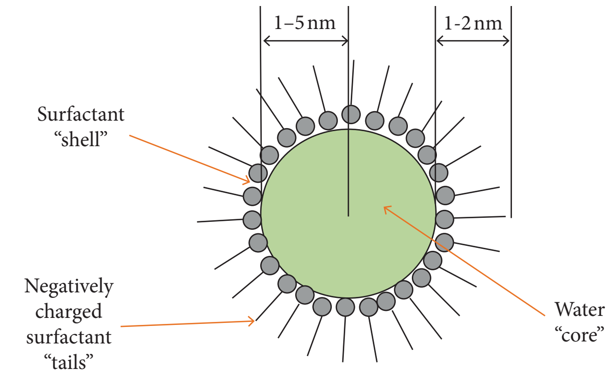

Figure 1: An emulsified water droplet (theoretical).

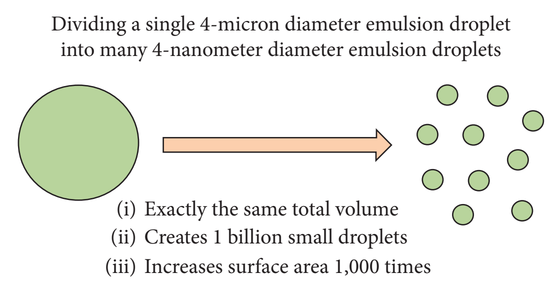

Figure 2: Reducing emulsified water droplet size.

is necessary when verifying testing fuel additives having a cumulative effect. For a general discussion on this matter, please refer to Section 5.1.3.3, page 14, from reference [15].

The determination of fuel economy for a fleet of "identical" vehicles to within a 3% accuracy (with a 90% confidence) required the testing of only 5 vehicles when driving over a suitable test track cycle compared to 14 vehicles for the laboratory chassis dynamometer cycle (see reference [16], page 170). This naturally implies that inevitable variability in fuel economy when operating under "real life" road conditions cannot be properly duplicated under strictly controlled stationary engine dynamometer testing. This variability in individual vehicle fuel economy results is the result of cumulative effects from differences in engines, fuels, drivers, maintenance, routes, loads, climate, fleet logistics, etc.

Therefore, it was decided to test the additive using multiple vehicle fleets comprising a robust sample of different vehicles being driven "over the road" under "real life" operating conditions. TNO Quality Services B. V. (now known as TUV Rhineland Quality) helped develop the testing protocol and also supervised the testing. An independent consultant was retained to collect data and analyze the impact of using the additive [17]. Consultant's conclusions were as follows:

(i) *"Ground vehicles considered in this analysis used approximately 475,000 litres of treated fuel and covered a total of 14 million kilometres using the fuel additive. The number of test vehicles (538), extensive* *testing period, and significant distance travelled gives great confidence in the result."*

(ii) *"The combined average weighted fuel saving due to using the fuel additive is calculated to be approximately 9.7%."*

Heavy duty diesel engine manufacturers included in the test were Mercedes, Volvo, Renault, DAF, Iveco, and Skoda. No engine or fuel system problems due to using the additive were reported during the testing period. Some fleets used Euro 4 diesel (50 ppm sulfur) and some used Euro 5 diesel (10 ppm sulfur).

The additive dose ratio was 8,000 : 1 by volume for all testing conditions. Dose ratios were always made by volume (not weight) since the additive uses volume to create surface area.

It was discovered during the fleet tests that apparently identical vehicles do not necessarily have exactly the same fuel economy changes when using the additive. Also, there was widespread variability in fuel savings, with some vehicles achieving significantly more fuel savings than others [17] (refer to Figure 3).

As can be seen from the above bar chart (Figure 3), approximately 34% of all tested vehicles had fuel economy savings of 7.5% to 10%. Also, approximately 14% of vehicles saved 12.5% to 15%.

It was also confirmed during testing that the additive has a typical conditioning delay period of about 8 or 10 weeks driving before fuel economy improvements become stable enough to accurately predict future fuel savings. Figure 4 illustrates the combination of variable performance and fuel saving delay for three different vehicles (*A*, *B*, and *C*). Additive dosing began at week zero.

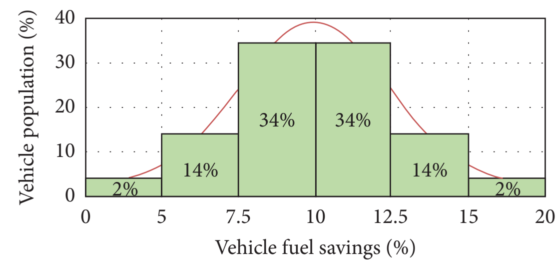

Figure 3: Vehicle fuel economy variability graph (speculative).

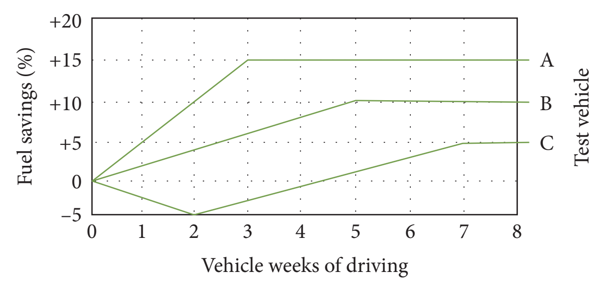

Figure 4: Fuel additive cumulative effect graph.

2.3. Additive Mechanism of Action (Speculative). Additive development was based on intuitive trial and error. Due to time and cost restraints, formally established, strict scientific methods were not followed (observation, hypothesis, experiment, data analysis, testing, modification of hypotheses, and repeat etc.). For this reason, any improvements in vehicle fuel economy could not properly be attributed to any specific verifiable scientific reason. However, as can be seen below, a reasonable basis exists to conclude the most likely reason for fuel economy improvements is due to surface catalytic action of the additive droplets on fuel combustion:

(1) Although classic "steam explosions" generated by water emulsion droplets within the fuel increases turbulence and promotes enhanced fuel atomization [11], this would not give enough of a benefit to account for the average 9.7% improvement in fuel economy [17]. This seems likely since most modern heavy duty diesel engines already have extremely high fuel injector pressures designed to promote atomization, turbulence, and improved air/fuel mixing.

(2) Commercially available diesel fuel typically contains about 100 to 150 ppm of "dissolved", or "free" water. This free water is not constrained within a surfactant shell (Figure 1) and would, therefore, not be subjected to any form of "steam explosions" [11]. Also, dissolved water displays no catalytic properties [10] and is, therefore, unable to benefit fuel combustion.

(3) Fleet testing [14] recorded fuel savings of 9.7% which is simply too large for such a benefit to be assigned to any kind of chemical reaction directly involving the fuel additive. At a dose ratio of 8,000 : 1 (or 150 ppm v/v), there is just too little additive mass to have sufficient direct involvement in the fuel/air combustion reaction.

(4) Considering the above, the most likely reason for the additive to show a 9.7% fuel economy improvement [14] is probably due to some kind of combustion catalytic effect attributable to the emulsified water droplets, such as that described in references [8–10].

(5) The additive contains only compounds of carbon (40%), hydrogen (10%), oxygen (47%), nitrogen (2%), and sulfur (1%). Percentages given are approximate. There are no metallic or organometallic combustion catalysts. Fuel additives containing metallic compounds [8, 9] can be toxic and are, therefore, illegal in most countries.

(6) Verified emulsion droplets having the majority of sizes less than 4 nanometers [14] clearly meet the requirement for catalytic combustion benefits described in reference [10] which describes how very small water droplets (typically 20 Angstroms, or 2 nanometers) can be highly catalytic to diesel fuel combustion.

(7) Classical catalytic effects are typically enhanced by a combination of increased surface area and surface proximity to the targeted chemical reaction:

(i) Dosing fuel with the additive typically creates multiple 4-micron diameter emulsified water droplets [14]. When dosed at 8,000 : 1, this creates about 3.7 billion, billion droplets per liter of fuel with a total catalytic surface area of about 190 square meters per liter. Assuming a typical 2 liter, 4 cylinder, automobile engine; each 500 cc cylinder requires an injection of about 0.052 ml of fuel per combustion cycle (assuming stoichiometric conditions). Even this small volume of fuel still contains sufficient emulsified water droplets to create a total catalytic surface area of about 100 square centimeters per combustion cycle (or about the same surface area a typical combustion chamber). *This satisfies the first catalytic requirement for maximized surface area.*

(ii) Creating a negative electrical charge on the exposed surfaces of fuel emulsion droplets will promote both their natural separation and consequently, even distribution throughout the fuel by natural polarity repulsion (Figure 1). This droplet repulsion applies not only to each other but also from any exposed metal surfaces such as the fuel tank and delivery system (vehicles typically have negative grounding from their battery). Evenly distributed 4 nanometer droplets in an 8,000 : 1 dose ratio fuel emulsion would all be only about 80 nanometers apart. Even at a dose ratio of 8,000 : 1, each catalytically active water droplet would be extremely close to its nearest neighbor (only 80 nanometers) and, therefore, close enough to influence all air/fuel combustion. *This satisfies the second catalytic requirement for maximized proximity.*

Therefore, it seems reasonable to conclude that vehicle fleet fuel economy improvements of 9.7% [17] are probably due to surface catalytic action of the nanoemulsified water droplets on fuel combustion since only a catalytically active additive could achieve this level of fuel savings from such a low dose.

3. Conclusions

Deliberately manipulating the relative proportions and quantities of the key ingredients used to produce the microemulsion fuel additive in order to effectively control the emulsified water droplet sizes and size distribution within the fuel as well as modifying the dose ratio to affect the per liter droplet catalytic surface area was the basis for the chronological development of the fuel emulsion additive technology. This technique being applied to a practical and useful fuel additive clearly distinguishes this additive from all other currently available emulsion fuel additive technologies.

In order to achieve significant environmental CO_2 reductions, any fuel additive that improves vehicle fuel economy must also be widely used. This requires an additive that can be easily dosed at any major fuel distribution terminal and has been proven to be safe and easy to use with no fuel storage, delivery, or infrastructure changes and requiring no vehicle modifications of any kind. To this end, a catalytically active, nonmetallic, ultralow dose, nanoemulsion fuel additive was developed and road tested for fuel economy improvements using multiple fleets of heavy duty diesel trucks.

An independent consultant was used to analyze all fuel economy data collected from a two-year test using 538 heavy duty diesel trucks from 15 different vehicle fleets. Fuel economy improvements were compared both with and without the additive operating under "real life" driving conditions. Vehicles in this test used 475,000 litres of treated fuel and covered a total of 14 million kilometres. Consultant's report showed a combined average weighted fuel savings of 9.7% [17].

Data Availability

The raw data used to support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this research article.

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