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Homogeneous Combustion Catalysts for Efficiency Improvements and Emission Reduction in Diesel Engines

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Abstract

The effectiveness of the use of the FTC/FPC diesel combustion catalysts manufactured by Fuel Technology Pty Ltd, in diesel fuel oil used in mining operations including haul trucks, light vehicles, and mobile equipment was evaluated by means of reviewing a large body of information found in the open literature and performing various proprietary field trials. It was found that the diesel combustion catalysts are capable of improving both fuel efficiency and engine performance, which is supported by both combustion theory and field trial data. A fuel reduction of 2.5% across all types of engines can be claimed with > 97% confidence based on statistical analysis. The catalysts can also improve the mechanical performance of engines due to cleaner combustion with much reduced soot and unburnt hydrocarbon formation.

Keywords: diesel engines, emissions, industrial explosives, fuel efficiency, homogeneous combustion catalysts, mining

1 Introduction

Australia's current diesel consumption is about 25 GL (billion litres) per annum [1] and BHPBilliton Iron Ore's operation in WA alone consumed ca. 350 ML (million litres) in 2006/07 [2]. This represents an enormous energy cost in Australia's economy and a huge greenhouse gas footprint. Any improvement in energy efficiency of engines fuelled on diesel will have significant implications in the nation's sustainable energy and economic development [3].

Diesel is dominantly used in mining operations (haul trucks, mobile equipment, locomotives as well as light vehicles), road transport, shipping and power generation in regional towns and remote communities, primarily in compression ignition (CI) engines [1-4]. The fuel efficiency in CI engines depends on, among other factors, the rate of combustion of the diesel and the peak flame temperature in the engine [4-12]. The diesel combustion process and mechanisms in the CI engines are complex and a combustion catalyst that can accelerate the burning process leading to shorter combustion times and higher peak flame temperatures, which improve the engine efficiency and thus reduce diesel consumption [4].

There are several diesel fuel additives on the market that are claimed to be able to improve diesel engine efficiency and reduce fuel consumption [1,12-17]. Among these are the picric salts of ferrous iron, as manufactured by Fuel Technology Pty Ltd in Australia [1,16], and cerium based additives, as marketed by OXONICA [14] as well as Shell's Cetane Number (CN) Enhancer diesel additive and many more [18]. In application, the additives are directly dosed into commercial diesel without the need to modify the engines at a ratios ranging from 1:16,000 to 1:5,000, depending on the "strength" of the catalytic ingredient in the additives [1,12-18]. It has been claimed that these diesel additives can deliver benefits including improved fuel economy, reduced engine emissions, lowered engine noise and much reduced carbon deposition in cylinders and on fuel injectors, therefore easing engine maintenance requirements [18]. However, the widespread use of these diesel additives has been hindered by the lack of *systematic* science-based understanding and proof of the efficacy of the use of the additives. This is because the "on-road" performance of a diesel engine depends on many factors, including [1,4,12,15,16,18]: (1) fuel related variables, (2) engine type, age and maintenance (3) road conditions, (4) weather conditions and, not the least, (5) the different operator (driver) habits.

These demand further investigations into the mechanisms and effectiveness of the diesel additives and optimisation of their formulations on a systematic scientific basis. The present contribution evaluates the use of the FTC/FPC diesel combustion additives manufactured by Fuel Technology Pty Ltd, in diesel fuel oil used in mining operations, based on a large body of information found in the open literature and performing various proprietary field trials.

2 Chemistry of FTC/FPC Diesel Additives

The FTC/FPC diesel additives are made from ferrous picrate with approximately 12% n-butanol, a complex mixture of short-chain alkyl benzenes (approx. 87%) and a small amount (approx 1%) of dioctyl adipate, a common plasticiser. The short-chain alkyl benzenes range from xylenes (C2 alkyl group) to tetramethylbenzenes (C4 alkyl group). As far as the fundamental chemistry goes, ferrous picrate needs to be dissolved in a solvent. An organic solvent or solvents are often used so that the solvents can form continuous phase with both picrate solution and diesel. Alcohols are the obvious choice as they can mutually dissolve with both water and hydrocarbons. Benzene or toluene and their derivatives are necessary additives that help improve the stability of the ferrous picrate-water-butanol-diesel solution.

Picric acid or Trinitrophenol is a potentially hazardous chemical [19,20]. It was formerly used as an explosive and is an intermediate in dye manufacture. It is also present in many laboratories, where it is used as a chemical reagent. Water is added to picric acid to act as a desensitizer. The wetted product is significantly less shock sensitive than the dry acid. Picric acid is highly reactive and, in the presence of metals, metal salts, bases, ammonia and even concrete, readily forms picrate salts, some of which are more sensitive explosives than the parent acid.

Diesel consists mostly of hydrocarbons ranging from C8 to C24 with majority falling in the range of C10 – C18 [21,22]. The composition of diesel may vary with changes in latitude or changes in season. This variability is provided by the refinery to control the volatility of the product. Diesel fuel has a flash point of 48 to 71 °C and flammability limits of 0.7% to

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5% in air under ambient conditions. The mechanisms of diesel combustion in compression ignition engines is complex and typically involves the following steps [1,4-12]:

1. Near **adiabatic compression** of the intake air in the cylinder to high temperature and pressure;
2. **Fuel injection** to form finely dispersed diesel droplets suspended in air within the cylinders;
3. **Ignition** of the diesel-air cloud occurs upon rapidly compression by the piston with, in vast majority of cases, each droplet forming its own *flame front or flamelet*;
4. In the **propagation** stage, the *flamelets* propagate through the entire diesel fume and air mixture as well as evaporate and burn the diesel droplets rapidly, releasing energy;
5. The **peak flame temperature** is reached when the fuel combustion completes and
6. As the fuel becomes exhausted, the combustion completes and the flue gas is subsequently discharged.

This completes a combustion cycle and the engine fuel efficiency depends on the peak flame temperature and the time to complete the combustion cycle. The rate of diesel combustion depends on a number of factors including droplet size, the number of droplets and therefore the *flamelets* and how quickly each of the *flamelets* burns [1,4-12]. The diesel additive improves fuel efficiency by acting on one or more of these factors. A homogeneous combustion catalyst that promotes the rate of burning at the *flamelet* level is considered beneficial [1,4-6,9,10].

A number of metal ions such as calcium, iron, cerium, copper, manganese, barium and most precious metals are known to promote hydrocarbon combustion. In order to use one of these ions as diesel combustion catalyst, the ions have to be "dissolved" in diesel so that it can be rapidly dispersed into the droplets. This also naturally requires the ions to be present in a salt that decomposes very rapidly upon heating and the salt or its solution is dissolved in the diesel and is not present as particulates (which cause wear and tear in the engine).

Therefore, ferrous picrate, as used by Fuel technology Pty ltd, is a good choice among the many possible options as it delivers the ferrous ions as the combustion catalyst and decomposes at an extremely high rate upon heating. In summary, the use of the FTC/FPC combustion catalysts as a diesel additive to improve engine energy efficiency has a sound scientific basis.

3 Review of Reported Laboratory Studies and Field Trials

There have been a number of laboratory studies and field trials on the FTC/FPC combustion catalysts and a concise summary of these studies can be found in [1]. It is therefore not intended to repeatedly summarise these studies and trial reports but concentrates on the evaluation of the methodologies employed in each study and applies a statistical analysis on the raw data produced in these studies to obtain the confidence level of the claimed reduction in diesel fuel consumption after the application of the diesel additive.

Reported test-work upon the use of the FTC/FPC combustion catalysts is often operating within the area of statistical inference. This problem results from a number of variables, as summarised in **Introduction**, and only some of which are controllable. Some major findings of laboratory and field trials are summarised in Table 1 below.

Table 1 Comment on Research or Testing Methodologies in Various Studies

Project Details	Comments on methodology	Raw Data Availability
WA Institute of Technology 1985 Laboratory testing using Varimax TD35 Test & Research Engine (diesel).	Laboratory-based stationery engine tests under best controlled conditions with fuel consumption and power output measured. The ambient temperature was not controlled which would affect the results. Fuel saving: 2.5% and power output: increased by 2%. The lower the efficiency of use (throttle / revs) the greater the saving.	Available for statistical analysis.
Southwest Research Institute, 1992 Lab testing using EMD Generator for power absorption	Laboratory stationery engine tests under controlled conditions with fuel consumption and power output measured. The ambient temperature was not controlled Fuel saving: 1.7%	Available for statistical analysis.
University of Western Australia, 2005 Laboratory Testing using 75 kVA and 100 kVA generator engines	Laboratory-based stationery engine tests with decent planning but the program did not seem to be well executed. Fuel savings: 3 – 5% on older engine but no clear effect on the newer engine, especially at full load.	Available for statistical analysis.
Fuel Technology Pty Ltd 2005 Field trials involving trucks (CAT 793) and mobile equipment using various methods.	Various methodologies were employed: Monthly Fuel Burn Trends: 2 x CAT992G ROM Loaders: <u>not detected due to natural variations and/or poor measurements</u> CAT 793 (T1581) VIMS Data: <u>2.6% fuel saving</u> Fuel Technology's Carbon Balance Method: <u>7.9% fuel saving</u> Specific Fuel Consumption Tests based on fuel records (Trucks 1269 & 1581): <u>4.8% fuel saving</u> In addition, significant improvement in "cleanness" of engines burning the additive treated diesel was observed.	Valuable results for bench marking against the statistical analysis.

4 Field Trials at BHP Billiton Mt Keith

The field trials undertaken at Mt Keith Operations (MKO) comprised of two main types:

a) Using general MKO data such as monthly volumetric fuel consumption trends, and Truck VIMS data.
b) More controlled specific fuel consumption tests.

Equipment provided for this fuel efficiency evaluation comprised of three Caterpillar 793 series trucks, Numbers

1269, 1326 and 1581. A calibrated catalyst-metering system was installed, allowing diesel fuel to be FTC/FPC treated at time of fuel transfer from bulk storage tanks to day tanks at refuelling bay, as shown in Figure 1 below.

Figure 1 FTC/PFC Diesel catalyst dosing system

The Specific Fuel Consumption (SFC) test procedure requires measurement of the mass of fuel consumed related to the work performed in hauling a measured load of ore over a defined distance. Trucks 1269 and 1581 were selected for the SFC test, which were conducted over a surveyed circuit marked out on the haul ramp in an area where no changes to the profile would occur over the test period. A start point was selected on a reproducible section of the ramp haul and windrow marked. A point near the top of ramp was defined as the end point of the haul route. The distance between these points was surveyed at 1.98km. The MacNaught Model M10 flow transducers coupled with thermocouple probes were connected to the truck's fuel tank outlet and return fuel pipelines. These transducers, which have been calibrated to $\pm$ 0.25% are connected to a KEP Minitrol Totaliser mounted in the truck cab. The thermocouple probes are connected to a dual reading digital thermometer, also mounted in the cab workstation. As the temperature of the fuel can vary relative to ambient temperature changes as well as increase significantly during a working shift, constant temperature monitoring is required to enable calculations of the mass of fuel consumed for each haul. Following the loading of the truck at each cycle, the truck was driven to the pit ramp marker and stopped. The Minitrol totaliser and stopwatch are zeroed. At the signal "*GO*" the driver accelerates and the test engineer activates the totaliser and stopwatch. The truck is driven at full throttle to avoid driver variables over the haul route. Fuel temperatures are recorded at the mid haul point. Upon arrival at the end marker the stopwatch and Minitrol totaliser readings are recorded.

The specific fuel consumption tests conducted on trucks 1269 and 1581 in such a working environment provided fuel savings of 6.2% and 3.7%, respectively. Figure 2 shows the typical results for truck 1269.

5 Statistical Analysis of Fuel Savings Data

The reported reductions in diesel consumptions due to the addition of the FTC/FPC combustion catalysts in various studies and field trials are so variable, ranging from negative up to 12% savings as claimed by some reports, that it is too difficult to make a final call on the actual level of fuel saving potential. A statistical method based on probability analysis to reduce potential statistical bias in the various testing data was devised and applied in this work. In brief, the analysis takes on the raw data presented and compounds them into two groups: the reference data group contains the performance data with un-treated diesel and the target data group contains the performance data with treated diesel, similar to that presented in Figure 2. Data in both groups are then sorted according to a complex set of test conditions under which the results were obtained. The difference between the reference and targeted groups under any chosen condition is computed as fuel saving at that point, expressed in percent relative to the reference data. A fixed set of targeted performance data, termed "Expected Fuel Reduction", is assigned and the frequency of occurrence of measured data fall within 1% of the assigned "Expected Fuel Reduction" value regardless the test conditions under which the data were obtained is taken as the statistical "Confidence", expressed in percent, in the "Expected Fuel Reduction". Recognise that there is a degree of uncertainty in the Conference value thus determined, a sensitivity analysis is then applied by artificially varying the Confidence value up and down until 10% variation in the measured data set has to be incorporated in order to sustain the assigned "Expected Fuel Reduction" value. The up and lower boundaries of the Confidence thus determined give the error bar as presented in Figure 3 below.

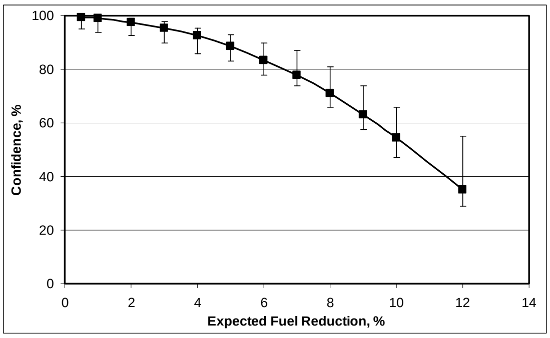

Figure 3 Statistical confidence vs expected fuel saving

The analysis involved some 27,000 data points and was a very laborious and time consuming process. However, the result is very neat and less subjective. The use of the statistical results has to involve a degree of subjectivity. For example, if 97% Confidence provides the comfort, then 2.5% reduction in diesel fuel consumption is the value to accept or, at 95% Confidence, 4.4% fuel reduction is acceptable. Likewise, for a claim of 12% fuel reduction, one would have to feel comfortable with ca. 34% Confidence, which for sure is hard for anyone who has to make the decision. The author wishes to recommend 2.5% reduction in diesel fuel consumption when treated with the FTC/FPC combustion catalysts with 97% Confidence.

6 Other Benefits

The field trials also confirmed that the FTC/FPC diesel catalysts can deliver other benefits including reduced engine emissions, lowered engine noise and much reduced carbon deposition in cylinders and on fuel injectors, therefore easing engine maintenance requirements, in addition to improved fuel economy. Inspection of engines operated on diesel dosed with the catalysts showed significantly reduced soot deposition in the cylinders and piston heads.

Recognising that diesel used in manufacturing explosives for mining operation is more logistically and conveniently drawn from the same tanks in which the diesel has been treated with the combustion catalysts, further laboratory tests showed that there is no noticeable difference in the performance of the ANFO made with normal diesel and the additive treated diesel. Therefore, it is confidently concluded that the additive treated diesel can be used to manufacture ANFO and various heavy ANFO explosives. The effect of the FTC/FPC combustion catalyst on the stability of emulsion explosives was also assessed and confirmed that the additives do not affect the stability and performance of the emulsion explosives.

7 Conclusions

The evaluation of the effectiveness of the FTC/FPC diesel combustion catalysts manufactured by Fuel Technology Pty Ltd, confirmed that the diesel additives are capable of improving fuel efficiency, which is supported by both combustion theory and field trial data. A fuel reduction of 2.5% across all types of engines can be achieved with 97% confidence based on statistical analysis. Furthermore, the additive doped diesel can also be used in manufacturing mining explosives (ANFO) without any noticeable side effect on the stability and performance of the ANFO.

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References

1. Zhang, D., "Fuel Efficiency Improvements", Internal Report, BHP Billiton Iron Pty Ltd (2007)
2. BHP Billiton Iron Ore Pty Ltd, "2006/2007 Annual Environmental Report" (2007)
3. CSIRO, "Climate Change in Australia" , Australian Greenhouse Office (2008)
4. Westbrook, C.K., ***Proceedings of the Combustion Institute***, Vol. 28, pp. 1563–157 (2000)
5. Nam, C.M. and Gibbs, B.M., ***Fuel***, Vol. 81, pp. 1359 – 1367 (2002).
6. Mi, H.H., et al, ***Chemosphere***, Vol. 41, pp. 1783 - 1790 (2000).
7. Hansen, A.C., et al, ***Bioresource Technology*** Vol. 96, pp. 277–285 (2005)
8. Razus, D., et al, ***Journal of Loss Prevention in the Process Industries*** Vol. 19, 334–342 (2006)
9. Jung, D and Assanis, D.N., Multi-Zone Di Diesel Spray Combustion Model for Cycle Simulation Studies of Engine Performance and Emissions, **SAE 2001 World Congress, March 2001**
10. Omote, H., Assessment of a Detailed Kinetic Diesel Combustion Model by In-Cylinder Optical Measurements, **SAE 2001 World Congress, April 2006**
11. Fino, D.; Specchia, V., ***Chemical Engineering Science***, 59(22-23):4825-4831 (2004)
12. Parsons, J. B. and Germane, G. J., The Effects of an Iron Based Fuel Catalyst upon Diesel Fleet Operation, **SAE Technical Paper Series 831204**
13. Greenhouse Gas Technology Center, "Verification Report EnviroFuels Diesel Fuel Catalyzer Fuel Additive", Southern Research Institute (2005)
14. OXONICA, "Catalysis: Catalytic Function of Cerium Oxide" (2005)
15. Su, F., et al, (Engine System Development Centre), "Simplified fuel additive test phase IV: Test Protocol", prepared for Transportation Development Centre, Transport Canada (2003)
16. Platt, R.A., "Reduction in Greenhouse Gas Emissions by Application of a Combustion Catalyst", Fuel Technology Pty Ltd (1999)
17. Shell "Multifunctional Diesel Fuel Additives" Shell Internal Report (2006)
18. Riley, T., "FPC Fuel Catalyst Trials at Mt. Keith", Fuel Technology Pty Ltd and BHPBilliton MKO, (2005)
19. Honda, K., et al, "Hexaaquairon(II) dipicrate dihydrate", Crystal Structure Communications, Vol C59, pp. 319 – 321 (2003)
20. Charlebois, P., ***Safety Scribe*** Vol 11, No. 2, University of Alberta (1997)
21. Fuel Standard (Automotive Diesel) Determination 2001, The Australian Commonwealth Government, Canberra (2001)
22. Fuel Quality Standards Bill 2000, The Australian Commonwealth Government, Canberra, 2000.

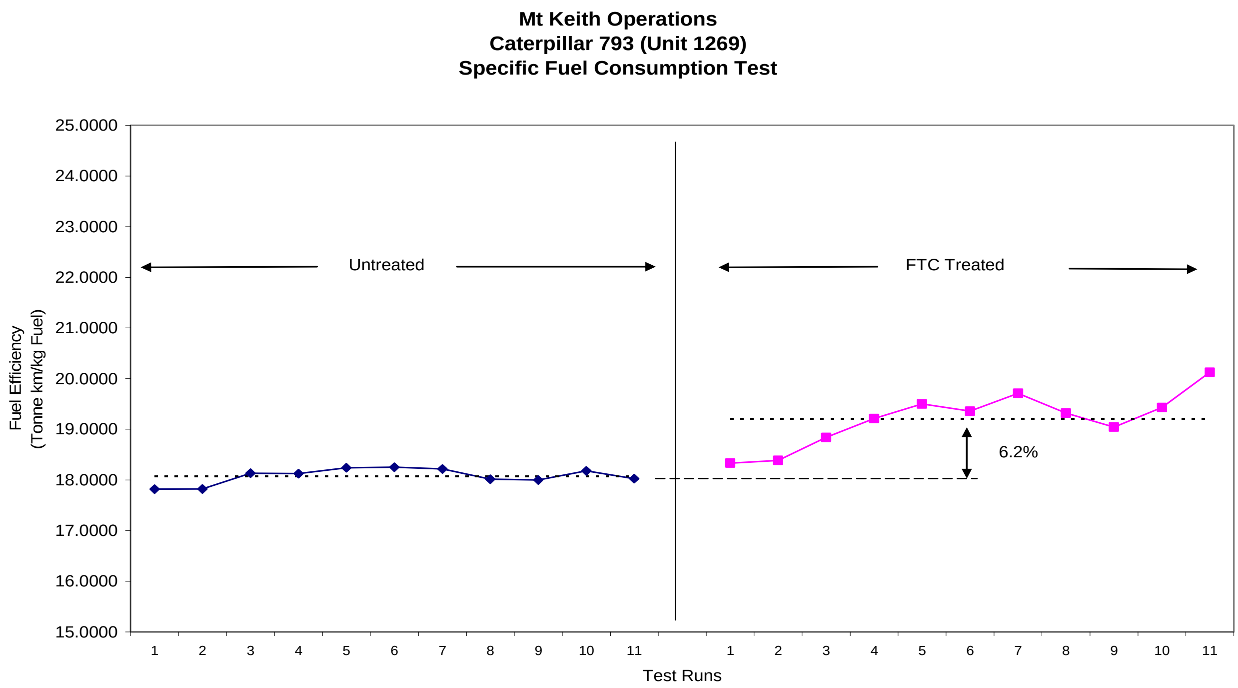

Figure 2 Typical results of specific fuel consumption tests at MKO