

Centre for Energy

"energy for today and tomorrow"

ARC LP0989368

"Homogeneous Combustion Catalysts for Efficiency Improvements and Emission Reductions in Diesel Engines"

Summary Report

Prepared for BHP Billiton Iron Ore Pty Ltd and Fuel Technology Pty Ltd by:

Winthrop Professor Dongke Zhang *FTSE* Dr Yu Ma Dr Mingming Zhu

28-03-2014





Project Overview

This report summarises significant breakthroughs in scientific understanding of a Homogenous Combustion Catalyst called FPC, from a four-year research programme at the Centre for Energy, The University of Western Australia (UWA).

The FPC catalyst, with the ferrous picrate as the active component, is manufactured and commercialised by Fuel Technology Pty Ltd (FTPL) in Western Australia. There have been a number of laboratory tests and field trials to ascertain the effect of FPC on the performances of diesel engines. In 2007, the need for better understanding of the underlying scientific principles and a higher level of academic rigour than was normally possible with field trials was recognised, leading to a collaborative research project between the Australian Research Council, BHP Billiton Iron Ore Pty Ltd, FTPL and UWA. Research commenced in 2010 and after four years, the outcomes are significant in three ways:

- Confirmation of the significant fuel saving and emission reduction benefits of using the ferrous picrate catalyst produced by FTPL;
- Improved understanding of the working mechanisms of the ferrous picrate catalyst in combustion and soot formation processes in diesel engines;
- Extension of the application of the catalyst to improving the combustion and emission characteristics of biodiesel from diesel engines.

Chemistry of FPC

The FPC homogeneous combustion catalyst is made from ferrous picrate with an organic solvent system, including picric acid, *n*-butanol and a complex mixture of short-chain alkyl benzenes (Recosol 100/150), as shown in Table 1. Ferrous picrate, the active ingredient, is produced from the reaction of picric acid and iron. Picric acid (2,4,6-trinitrophenol) is a highly reactive chemical, which has been primarily used as an explosive and is an intermediate in the dyeing industry. Dry picric acid appears as a yellow needle-like material and is highly sensitive to heat, shock and friction, so water is added during transportation/storage to act as a desensitiser. This water is then



removed during the formulation of FPC. Ferrous picrate is even more sensitive and explosive than the parent picric acid although it should be noted once dissolved in the solvents as used in manufacturing FPC, explosiveness is negated.

The manufacture-finished ferrous picrate catalyst is a dark green-coloured solution ready for use by dosing in diesel in appropriate dosing rate. FPC has the following distinct characteristics:

- Solubility in diesel fuel without precipitation or agglomeration during handling, storage or consumption.
- Excellent catalytic activity in promoting combustion so that only a very tiny amount of the catalyst is required.
- No change to the fuel specification and does not generate secondary pollution problems.



Table 1 Major components in FPC and their physical properties

Component	Content	Organic compound	Molecular weight (g/mol)	Density (g/ml, 20°C)	Flash point (°C)	Boiling point (°C)	Vapour pressure ¹ (kPa, 20°C)
Recosol 150-		Naphthalene	128		62-65.6	158-214	
Solvent naphtha (petroleum),	10~60%	1,3,5-trimethylbenzene	120	0.88-0.91			< 1.3
heavy aromatic		1,2,4-trimethylbenzene	120				
		1,3,5-trimethylbenzene					
Recosol 100-		1,2,4-trimethylbenzene	120	0.87-0.88	38-47	148-182	0.8
Solvent naphtha (petroleum),	< 10%	1,2,3-trimethylbenzene	120				
light aromatic		n-propyl benzene, cumene					
		xylene and isomers	106				
n-butanol	< 10%	n-butyl alcohol	74	0.81	35	117.7	0.56
Picric acid	< 10%	2,4,6-trinitrophenol	229	1.8	150	300 ²	0.1kPa at 195°C
Iron picrate	< 10%	Phenol 2,4,6-trinitro-, iron(²⁺) salt	512	-	-	250 ²	-

Note: 1. Vapour pressure is an indication of a liquid volatility. A substance with a high vapour pressure at normal temperatures is often referred to as volatile; 2. Referring to the decomposition temperature of the compound.



Results of Laboratory Engine Tests

The effect of the FPC catalyst on the performance of diesel engines was systematically tested using a four-stroke, single cylinder, direct injection engine (YANMAR L48AE, AET Ltd) under precisely controlled laboratory environmental conditions at the Centre for Energy at UWA. The engine had a 70mm bore, 55mm stroke, 211cm³ displacement and compression ratio of 19.9:1. A water-cooled, electric dynamometer was coupled to the engine shaft to provide the load conditions. Caltex No.2 diesel sourced from a local service station was used as the reference diesel fuel. The results of a long term testing programme provide clear scientific evidence of the multifaceted improvements with the use of the FPC catalyst, including:

- reduced brake specific fuel consumption
- reduced greenhouse gas emissions
- reduced exhaust particulate emissions (smoke)

Improved Combustion Efficiency

The brake specific fuel consumption is a recognised measure of fuel efficiency. Figure 1 illustrates a summary of the effect of the catalyst on the brake specific fuel consumption at full load, with varied engine speed and catalyst dosage.

For each data set in Figure 1, the left-most point represents results from the reference diesel fuel with no FPC addition. Increasing catalyst dosage along the X-axis produces a consistent trend of improved fuel combustion efficiency.





Figure 1 Brake specific fuel consumption at full load conditions and variable catalyst dosage

It was found the engine load plays a critical role in determining the efficacy of the catalyst in diesel engines. Figure 2 illustrates the brake specific fuel consumption results at the engine speed varied from 2800 to 3600 rpm and under variable load conditions. It is obvious that the use of FPC reduced the brake specific fuel consumption under all tested engine conditions.

Moreover, it is evident that the effect of FPC is more obvious when the engine was operated under light loads. As the engine load increases, the influence of the catalyst on the brake specific fuel consumption becomes less significant. As an example, at 2800 rpm, the catalyst reduced the fuel consumption from 573.1 to 548.9 g·kW⁻¹h⁻¹, a 4.2 % fuel saving at a light load, but as load (pressure) increases, the benefit was reduced to something in the region of 2.5%. This is because the gas temperature in the cylinder is higher when the engine load is higher, leading to a better burning condition of the fuel/air mixture. Consequently, the ability of the catalyst to improve the diesel combustion processes at higher engine loads is not as big as that at light engine loads, but is still of significant impact at, say, 2.5% fuel saving.





Figure 2 Brake specific fuel consumption at the engine speeds of 2800, 3200 and 3600 rpm and varying load conditions



Reduced Gas Emissions

Carbon monoxide (CO) is toxic to humans and animals and is a product of incomplete combustion of any carbon-based fuels. Figures 3 a – c illustrate that the CO emissions are significantly reduced when the FPC catalyst is added to the reference diesel fuel (termed 'RD'). Importantly, this is true across a wide range of engine loads, represented here as Brake Mean Effective Pressure (BMEP). The trend in CO emission reductions is similar at various engine speeds ranging from 2800 to 3600 rpm. The greatest CO reductions achieved by the addition of the FPC catalyst were in the order of 19% to 22%.

The presence of unburned hydrocarbons (UHC) in the exhaust also reflects incomplete combustion and environmentally damaging emissions. The pattern for the UHC reduction, as illustrated in Figures 4 a - c, is very similar to that for CO. The highest UHC reduction of 15% was achieved at lower engine speeds.







Figure 3 Carbon monoxide reductions by FPC at various engine conditions







Figure 4 Unburned hydrocarbon (UHC) reductions by FPC at various engine conditions

Reduced Diesel Particulate Matter

Diesel particulate matter (DPM) typically comprises of agglomerated primary soot particles with absorbed unburnt hydrocarbons and inorganic matter on their surfaces. These emissions, commonly known as soot, have a surprising range of adverse impacts on human health and the environment. During the course of this investigation, the regulation limiting the DPM or soot emissions from diesel engines was progressively tightened. Since November 2013, a more stringent Euro 5 emission standard has been applied to heavy-duty diesel engines in Australia, which regulates the smoke (soot) emissions at the rate of 0.5 m^{-1} .



The research also revealed that smoke emissions (DPM's), measured as smoke opacity, were drastically reduced by the addition of the FPC Catalyst. Figure 5 illustrates that the smoke emission was reduced with increasing catalyst dosage where RD is "Reference Diesel". The smoke opacity test results showed 7.3 to 39.5% reduction in the overall soot emissions when the catalyst was applied, depending on the catalyst dosage ratio and engine duty. It is interesting to note that the catalyst was more effective at both the upper and lower engine speeds, particularly the latter.

Visually, the soot reduction with increased catalyst dosage can be evidenced in the Transmission Electron Microscopy (TEM) imaging analyses of soot samples as presented in Figures 6 a – c. The irregularly shaped soot aggregates were composed of a number of very spherical primary particles. Comparing the three TEM images of the soot samples from the reference diesel and the FPC dosed fuels, a general trend can be seen that a significantly less amount of particles were deposited on the TEM grids for the FPC treated fuels than for the reference diesel under the same sampling conditions, suggesting that less soot was formed when the FPC catalyst was used. This is consistent with the observation of reduced smoke emissions as shown in Figure 5.



Figure 5 Reductions in soot emissions (opacity) using FPC Catalyst relative to Reference Diesel





Figure 6 TEM images of soot particles from the reference diesel (a), and diesel dosed with FPC at ratios of 1:10,000 (b) and 1:1,000 (c), respectively

Results of Large-scale Engine Tests

The efficacy of the ferrous picrate catalyst in improving diesel combustion was further examined using a large-scale diesel engine facility in this project. The diesel engine used in this test program was a Caterpillar R1700 turbocharged engine coupled with an eddy-current dynamometer. This engine was selected because it represents a large amount of heavy-duty diesel engines currently used in the underground mining loader for which the catalyst is intended to be applied. The engine was located at Mining Equipment Spares (MES) Pty Ltd. Table 2 shows the effect of the catalyst on the fuel efficiency improvements and exhaust reductions.

	CO		UHC		Fuel savings	
Engine condition	1400rpm	1800rpm	1400rpm	1800rpm	1400rpm	1800rpm
25% load	7.3%	14.9%	6.8%	13.3%	4.8%	5.6%
50% load	13.8%	20.7%	12.3%	22.8%	2.6%	2.6%
75% load	6.8%	9.1%	13.5%	5.8%	1.8%	2%
100% load	11.2%	10.0%	4.8%	2.3%	1.3%	1.1%

Table 2 Effect of the FPC catalyst on fuel efficiency improvements and exhaust reductions

From Table 2, it can be seen that the use of the FPC catalyst significantly promoted the diesel combustion under all tested conditions, with fuel savings ranging from 1.1% to 5.6%, CO reductions ranging from 7.3% to 20.7% and UHC reductions ranging from 2.3% to 22.8%. It is also noted that the effect of the catalyst on the brake specific fuel consumption was greater under lower engine loads than under higher engine loads, consistent with the laboratory engine tests.

Results of Engine Tests Using Biodiesel

In order to evaluate if the beneficial effects of the FPC catalyst could also be realised for biodiesel, a fuel that is increasingly gaining popularity, a set of four fuels was tested under controlled engine conditions, namely, reference diesel, diesel with FPC at a dosing ratio of 1:10000, a reference biodiesel obtained from BioWorks Australia Pty Ltd, and biodiesel with FPC at a dosing ratio of 1:10000. The dependency of the brake specific fuel consumption on the engine load (BMEP) with the engine operating with the four fuels at the engine speed of 3200rpm is presented in Figure 7. The brake specific fuel consumptions of biodiesel were greater than that of diesel, due to the lower heating value of biodiesel than that of diesel. It is also seen that the addition of the catalyst reduced the brake specific fuel consumption of both diesel and biodiesel, indicating that the catalyst promoted the combustion process regardless of which fuel was used in the engine. With the addition of FPC, a high fuel saving of 2.8% was obtained for the biodiesel combustion at the load of 0.4MPa BMEP.





Figure 7 The brake specific fuel consumption as a function of the engine load (BMEP)

The addition of FPC in biodiesel was also effective in reducing the CO and UHC emissions, as observed in Figures 8 and 9. Under the tested conditions, the reduction ratios of CO and UHC ranged from 4.2~17.3% and 2.5~3.8%, respectively. Note that the CO level from the untreated biodiesel was lower than that of the reference diesel under the low and medium load conditions, due to the extra oxygen content in the biodiesel and thus more complete combustion than the conventional diesel. However, CO was deteriorated from the load of 0.33MPa BMEP and upwards for the biodiesel fuel. This can be explained by that the air-fuel mixing process was affected by the difficulty of biodiesel atomisation because of its higher viscosity and density, together with the fact that less air was available when more fuel was injected to the engine cylinder at higher loads, resulting in locally fuel-rich mixtures and therefore more CO formation.





Figure 8 Carbon monoxide reductions by FPC under various engine conditions



Figure 9 Unburned hydrocarbon reductions by FPC under various engine conditions

Figure 10 illustrates the smoke emission levels from the fuels tested at the engine speed of 3200rpm and four load conditions. It can be seen that the smoke emission from biodiesel was lower than that from diesel due to the extra oxygen content in the biodiesel molecule. It was also noted that the smoke emission was further suppressed by the addition of FPC under all tested conditions. Compared to that of the untreated biodiesel, the smoke from the FPC dosed biodiesel was reduced by $11.5 \sim 24.4\%$.





Figure 10 Reduction in soot emissions (opacity) from biodiesel combustion using FPC Catalyst

Mechanisms of the FPC Catalyst in Fuel Combustion Processes

The combustion efficiency of a diesel engine depends on the peak flame temperature and the time to complete the combustion. The rate of diesel combustion is determined by a number of factors such as the droplet size and the degree of fuel-air mixing. The catalyst improves fuel efficiency by acting on one or more of these factors. Figure 11 illustrates the effect of FPC on the combustion characteristics of diesel in a diesel engine. These combustion characteristics include cylinder pressure, heat release rate, ignition delay and combustion duration. It is evident that FPC was capable of increasing the peak cylinder pressure and heating release rate, promoting diesel ignition and reducing the duration of diesel combustion. Based on the laws of thermodynamics, a faster burning rate in diesel engine results in a higher fuel efficiency.







Figure 11 Effect of FPC on the combustion characteristics of diesel at the engine speed of 3200 rpm and varying load conditions

Another way of evaluating this accelerated heat release is to measure the rate of combustion of a single droplet of the fuel under systematically controlled conditions. When a fuel droplet is exposed to a hot oxidising environment, it absorbs heat, vaporises and if the temperature is high enough, ignition occurs and fuel burning commences and continues until the fuel in the droplet is consumed. Figure 12 compares the burning rates and flame temperatures of diesel and biodiesel droplets dosed with the catalyst at various air temperatures. It is evident that the addition of the FPC catalyst increased the burning rates and flame temperatures of both fuels. For example, at 973K, the burning rate increased from 0.83mm²/s to 0.88mm²/s for the diesel and from 0.97mm²/s to 1.06mm²/s for the biodiesel, and the flame temperatures of the diesel and biodiesel droplets rose by around 40K, with the catalyst added at the ratio of 1:10000.





Figure 12 Effect of FPC on burning rate (a) and flame temperature (b) at various air temperatures

It was found that the boiling points of both diesel and biodiesel were higher than the decomposition temperature of ferrous picrate (523K). Therefore, the mechanism of the ferrous picrate in the combustion process of diesel and biodiesel is proposed as follows: upon heating, the surface temperature of the fuel droplets increases till reaching their boiling points. When the surface temperature of the droplets of the fuel with FPC treatment is higher than 523K, the ferrous picrate decomposes and releases iron atoms into the reaction zone, which promotes the oxidation of the fuel vapour. This results in higher reaction rates and an increase in the flame temperature of the increased flame temperature, resulting in a higher burning rate and a shorter burnout time. Overall, the fuel combustion efficiency is improved by the ferrous picrate catalyst.





Mechanisms of the FPC Catalyst in Soot Formation Processes

Figure 13 Weight loss curves of soot oxidation in air

Figure 13 illustrates the thermal behaviour of soot particles from the combustion of the four fuels tested, including reference diesel (termed "RD"), reference biodiesel (termed "BD"), and their respective FPC treated derivatives, as tested in the thermo-gravimetric analyser (TGA). As marked on the plots, three major mass loss events are clearly noticeable, corresponding to the evaporation and desorption of light hydrocarbons on the soot surfaces (Peak 1), oxidation of heavy hydrocarbons attached to soot (Peak 2) and the dry soot oxidation (Peak 3). For the last event, it is noted that the soot from the FPC treated fuels was ignited at a lower temperature and the oxidation was completed sooner. This indicates that iron in FPC deposited on the soot during combustion and subsequently catalysed the oxidation of the soot of both diesel and biodiesel.

Using the Transmission Electron Microscopy imaging technique and theoretical equations, the sizes of soot particles were obtained as shown in Table 3. It is noted that the sizes of primary soot $(\overline{D_p})$ and aggregates $(\overline{D_g})$ from the diesel and biodiesel with FPC treatments were consistently smaller than those from the untreated diesel and biodiesel fuels, respectively. This suggests that the fuel combustion was substantially enhanced by FPC, resulting in less soot precursors in the combustion zone and therefore the smaller primary soot and aggregates in sizes.



Table 3 Comparison of the sizes of primary soot particles and soot aggregates from the fuels with and without FPC treatment

	D _p (nm)	D _g (nm)
RD soot	24.5±0.4	295±6
FPC-D (1:10000) soot	23.5±0.4	283±5
BD soot	23.1±0.3	202±4
FPC-B (1:10000) soot	22.5±0.3	186±4

Note: $\overline{D_p}$ is the average diameter of the primary soot particles; $\overline{D_g}$ is the average gyration diameter, representing the average size of the soot aggregates.



Figure 14 A schematic of the mechanisms of FPC in the soot formation processes

The mechanism of FPC affecting the soot formation processes was thus proposed, as illustrated in Figure 14. The addition of FPC promotes diesel and biodiesel combustion by increasing the burning rate, flame temperature and shortening the burnout time, leading to more complete combustion of gas-phase hydrocarbon fragments and less soot precursors to form the primary soot particles, thus the smaller sizes of the primary soot and aggregates. Then the FPC actively accelerates the oxidation of the soot formed, as indicated by the lower ignition temperature and faster oxidation reaction. Following the aforementioned mechanism, the diesel and biodiesel combustion in a diesel engine is substantially improved by the FPC catalyst, resulting in reduced fuel consumptions and less overall soot emissions.



Conclusions

The evaluation of the effectiveness of the ferrous picrate based diesel combustion catalyst manufactured by Fuel Technology Pty Ltd has confirmed that the catalyst is capable of improving fuel efficiency, which is supported by both laboratory diesel engine tests and field trial data. Furthermore, the addition of the catalyst in the diesel and biodiesel can significantly reduce the emissions of smoke, unburned hydrocarbon and carbon monoxide.

It has been scientifically proven that the ferrous picrate decomposes and releases iron atoms into the flame zone during the combustion process of the droplets. The combustion rate is enhanced by the iron atoms in the flame, resulting in a higher flame temperature. Consequently, the heat transfer between the flame front and the diesel droplet surface is improved and the higher burning rate of diesel in the engine leads to higher fuel efficiency.

The improved combustion by FPC also leads to more complete combustion of the gas-phase hydrocarbon fragments and less soot precursors to form the primary soot particles. Therefore, the smaller sizes of the primary soot and aggregates are observed when using FPC. At the later stage of combustion, FPC actively accelerates the oxidation of the soot formed, resulting in a significant reduction in the overall soot emissions from CI engines.

Scientific Publications

The four-year UWA test programme has resulted in numerous reports and peer reviewed scientific papers published in internationally renowned journals as listed below:

 ZHANG, D. Homogeneous combustion catalysts for efficiency improvements and emission reduction in diesel engines. In: 7th Asia-Pacific conference on combustion, 24-27 May 2009, Taipei, Taiwan.



- ZHU, M., MA, Y. & ZHANG, D. The role of Homogeneous Combustion Catalysts in Diesel Combustion in Compression Ignition Engines. In: Australian Combustion Symposium, 2-4 Dec 2009, Brisbane, Australia.
- ZHU, M., MA, Y. & ZHANG, D. 2011. An experimental study of the effect of a homogeneous combustion catalyst on fuel consumption and smoke emission in a diesel engine. Energy, 36, 6004-6009.
- MA, Y., ZHU, M. & ZHANG, D. Evaluation of an Iron-based Organometallic Combustion Catalyst for Reduction of Exhaust Emissions from Diesel Engines. In: Australian Combustion Symposium, 29 Nov-1 Dec 2011, Newcastle, Australia.
- ZHU, M., MA, Y. & ZHANG, D. Effect of a Homogenous Combustion Catalyst on the Combustion Characteristics of single droplets of diesel and biodiesel. In: Australian Combustion Symposium, 29 Nov-1 Dec 2011, Newcastle, Australia.
- 6. ZHU, M., MA, Y. & ZHANG, D. 2012. Effect of a homogeneous combustion catalyst on the combustion characteristics and fuel efficiency in a diesel engine. Applied Energy, 91, 166-172.
- MA, Y., ZHU, M. & ZHANG, D. A Morphological Study of Soot from a Diesel Engine Fuelled with Diesel and Biodiesel. In: ACMM22/ ICONN 2012 /APMC10, 5-9 Feb 2012, Perth, Australia.
- MA, Y., ZHU, M. & ZHANG, D. The Effect of a Homogenous Combustion Catalyst on the Emission Characteristics from a Compression Ignition Engine Fuelled With Biodiesel. In: 4th International Conference on Applied Energy, 5-8 Jul 2012, Suzhou, China.
- ZHU, M., MA, Y. & ZHANG, D. Effect of a Homogenous Combustion Catalyst on Combustion Characteristics and Fuel Efficiency of Biodiesel in a Diesel Engine. In: 4th International Conference on Applied Energy, 5-8 Jul 2012, Suzhou, China.
- ZHU, M., MA, Y. & ZHANG, D. A theoretical investigation into the effect of a homogeneous catalyst on combustion characteristics of single droplets of diesel and biodiesel. In: 40th Australasian Chemical Engineering Conference (CHEMECA), 23-26 Sep 2012, Wellington, New Zealand.
- ZHU, M., MA, Y. & ZHANG, D. 2013. The effect of a homogeneous combustion catalyst on the combustion characteristics of single droplets of diesel and biodiesel. Proceedings of The Combustion Institute, 34, 1537-1544.



- ZHANG, D., MA, Y. & ZHU, M. 2013. Nanostructure and Oxidation Properties of Soot from a Compression Ignition Engine: The Effect of a Homogeneous Combustion Catalyst, Proceedings of The Combustion Institute, 34, 1869-1876.
- MA, Y., ZHU, M. & ZHANG, D. 2013. The Effect of a Homogeneous Combustion Catalyst on Exhaust Emissions from a single Cylinder Diesel Engine, Applied Energy, 102, 556-562.
- MA, Y., ZHU, M. & ZHANG, D. The Fate of Iron in a Homogeneous Diesel Combustion Catalyst in Compression Ignition Engines. In: Australian Combustion Symposium, 6-8 Nov 2013, Perth, Australia.
- MA, Y., ZHU, M. & ZHANG D. 2014. Effect of a Homogeneous Combustion Catalyst on the Characteristics of Diesel Soot Emitted from a Compression Ignition Engine. Applied Energy, 113, 751-757.

Submitted Publications

- 16. MA, Y., ZHU, M. & ZHANG, D. Effect of a Homogeneous Combustion Catalyst on the Nanostructure and Oxidative Properties of Soot from Biodiesel Combustion in a Compression Ignition Engine. Submitted to: 35th International Symposium on Combustion, 3-8 Aug 2014, San Francisco, USA.
- MA, Y., ZHU, M., ZHANG, D. *et al.* Understanding the Fate of Iron from a Ferrous Picrate based Homogeneous Catalyst during Diesel Combustion. Submitted to: 35th International Symposium on Combustion, 3-8 Aug 2014, San Francisco, USA.
- ZHU, M., MA, Y., ZHANG, D. *et al.* Effect of oxygenates addition on the characteristics and soot formation during combustion of single droplets of a petroleum diesel in air. Submitted to: 35th International Symposium on Combustion, 3-8 Aug 2014, San Francisco, USA.

Copies of all reports and papers are available on request.