The Role of Homogeneous Combustion Catalysts in Diesel Combustion in Compression Ignition Engines

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Abstract
This literature study examines the effects of various homogeneous combustion catalysts on diesel combustion in compression ignition engines. The catalyst is dissolved in diesel homogeneously to play the catalytic role during the engine combustion process. For example, Fuel Technology Pty Ltd's FTC diesel additives are iron based diesel combustion catalysts which are shown to have significant, albeit varying, benefits in both fuel saving and emissions reduction by various laboratory tests and field data. In this paper, the performance of the FTC/FPC diesel additives are compared with those of several other various commercial catalysts. How the catalysts act in each of key steps of diesel combustion process is then discussed building on an analysis of the mechanisms of diesel combustion in compression ignition engines. This review also highlights a number of technical and scientific questions that require further detailed and systematic research.

Keywords: homogeneous combustion catalysts diesel engines mechanism

1. Introduction

Diesel engines are dominantly used in heavy duty industries and increasingly hold their position in light duty vehicles. However, the strict requirements on both engine efficiency and emissions propose new challenges for their development [1]. Adding additives into diesel without modification of the engines is considered to be beneficial to engine performance such as reducing pollutant emissions and improving engine efficiency [2, 3, 4]. The catalysts are dissolved into the diesel homogeneously to play a catalytic role during diesel combustion in engines and they are said to pose no explosion hazards at low concentration of say 20ppm. Therefore, these additives are alternatively called homogeneous combustion catalysts.

There are two types of homogeneous combustion catalysts: metal-containing compositions and ash-less additives. Compared to the ash-less compounds, metal-containing compounds are considerably more effective even with lower concentration in the fuel [5]. A number of metal ions such as Iron [4, 6, 7], Cerium [3], Platinum [8], Copper [9], Sodium [10], Barium [11] and Manganese [12] are proven to promote hydrocarbon combustion. In order to use one of these ions as combustion catalyst, these catalysts have to be miscible with diesel and have no significant effect on fuel properties and decompose rapidly upon heating or combustion.

The combustion of diesel dosed with homogeneous catalysts is so complicated that there are limited studies in existence about their mechanisms in diesel combustion such as ignition, flame formation and propagation. The major study of homogeneous combustion catalysts was confined to their effects on engine performance [6, 7, 12]. This study reviews the performance of the homogenous combustion catalysts in diesel engines based on a large body of published literature. How the catalysts act on key steps of the diesel combustion process is then discussed in detail building on an analysis of the mechanisms of diesel combustion in compression ignition engines. Finally, a number of technical and scientific questions that require further detailed and systematic research are highlighted.

2. Performance of Homogeneous Combustion Catalysts in Diesel Engines

There are many commercial products like "Pt plus series" marketed by the Clean Diesel Technology in America, Envirox^{TM}(CeO_2) marketed by Oxonica Company in England and FTC/FPC catalysts produced by Fuel Technology Company in Australia. All these catalysts are claimed to deliver benefits including improved fuel economy, reduced emissions and carbon deposition in cylinders based on laboratory and field trial tests. Although the data are discrepant, fuel efficiency improvements of up to 12% have been reported [3, 4, 5].

FTC/FPC catalysts are ferrous picrate containing homogeneous combustion improver. They are proven to improve engine efficiency by faster and more complete combustion based on field and laboratory tests [4]. They are also claimed to have positive effects on the engine performance such as less abrasive wear and carbon deposit and no detrimental effects on fuel physical properties. Figure 1 summarises the results of specific fuel consumption improvement based on mining sites operation in Australia when the catalysts are applied. It can be seen that minimum specific fuel consumption improvement among field tests is 4% which is remarkable for diesel engines combustion. However, due to the complexity of diesel engine combustion which

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varies with engine types, engine speed and load, road conditions, air temperature and humidity, these discrepant data hinder the widespread application of the catalysts. Built on laboratory raw data involving more 27,000 points, Zhang [4] used a statistical method to establish a statistical confidence over the expected fuel reduction. It is founded that 97% confidence can be achieved when 2.5% reduction in fuel consumption is expected in diesel combustion treated with the FTC/FPC combustion catalysts.

There are conflicting results about the effect of the homogeneous combustion catalysts on NOx. Zeller et.al [7] claimed that ferrocene as an additive enhanced catalytic oxidation causing higher NOx emission. However, Du et.al [12] concluded that the NOx emission declined as the peak combustion temperature decreased when 25ppm ferrocene was added into the diesel fuel. When Parsons et.al [6] reported that the NOx emission could be reduced with working of the ferrous picrate based catalyst while Zeller et.al [7] pointed that ferrous picrate containing catalysts has little effect on NOx emission. However, the claimed reduction of NOx is inconsistent with the well-established combustion theory which is NOx emission increases with increasing engine efficiency. Results about the effect of homogeneous combustion catalysts on unburned HCs are also controversial. It was reported that unburned hydrocarbon emissions increased when ferrous based homogeneous combustion catalyst was applied in diesel engine [6] as well as fuel additive MMT was added into gasoline engine [13]. However, reduction in unburned HC in the range of 27%-61% was found using Pt based catalysts [14].

It has been recognised that homogeneous combustion catalysts are capable of reducing particulate matter. Before soot precursors occur, metal-containing additives dissociate and liberate metal atoms which condense to fine metal oxide aerosols. These oxides either deposit onto carbon particles or combines with the carbon particles to play a catalytic role late in the combustion process [15]. However, it is also arguable that soot suppression may occur in the early combustion stage where catalysts inhibit the soot precursors' formation [16]. Therefore, further study on the effect of the catalysts on soot formation process is needed.

3. Mechanism of Homogeneous Combustion Catalysts in Diesel Engines

Combustion of diesel in compression ignition engines invloves fuel injection, ignition, flame formation, propogation and extinction which is so complex that the mechanism of the diesel combustion with addition of homogeneous catalysts are more complicate. There exists some hypothesis about the mechanisms of the working of the catalysts in diesel combusiton until now built on the performance of the catalysts in diesel engines experiments while a definitive conclusion is lacked.

First of all, it is postulated that homogeneous combustion catalysts affect diesel ignition and combusiton rate [4,6]. Ignition plays a critical role in diesel engine operation as it determines whether the engine operates smoothly and fuel combusts efficiently. Linteris and Babushok [17] examined the effect of iron-containing additives $Fe(CO)_5$ on hydrogen ignition by using numerical calculation. It was found that $Fe(CO)_5$ has the same effectiveness with Fe at low additive volume fraction implying that $Fe(CO)_5$ decomposes to Fe relatively quickly and Fe reacts with oxygen producing a source of radicals O atom at the initial reaction stage. The same tendency about the effect of $Fe(CO)_5$ on methane and ethane ignition was also obtained in shock-tube experiments [18,19]. It was evident that the addition of small amount of $Fe(CO)_5$ promotes the ignition of methane while inhibits the ignition of ethane. Bobolev et.al [20] studied the action of iron catalysts on the combustion of solid ammonium perchlorate (AP) particle. Catalysts were Fe, Fe_2O_3 and Ferrocene. Measurements on the combustion rate and flame temperature indicated that all catalysts enhanced combustion rate and flame temperature. It was also observed that the effectiveness of all the catalysts increases with the increase in pressure. It is postulated that the mechanism with the iron catalysts could be the conversion of Fe and Fe_2O_3 to FeO. All these reactions are exothermic accelerating the overall combustion process. However, it is doubtful that whether this is effective when the catalysts are applied in diesel combustion as diesel has unique physical and chemical properties.

The second hypothesis is that nano-particles formed during diesel combustion treated with the metal-containing catalysts play a role of promoting fuel combustion at the final stage of engine process. It has been revealed that $Fe(CO)_5$ can form iron nano-particles rather than producing free radicals when its concentration added into fuel exceed a critical value [16]. Iron oxide nano-particles are also said to be an promising catalyst in promoting unburned hydrocarbon and carbon monoxide combustion [21] when they are coated on the surface of diesel after-treatment devices. Meanwhile, engine mechanical performance is claimed to be improved in terms of engine efficiency and pollution emissions when diesel is treated with nano-particle CeO_2 [3]. All these observations imply that it is possible for homogeneous combustion catalysts to form nano-particles during combustion and these particles promise to play catalytic role at the end of the fuel burn enhancing engine performance.

Apart from the viewpoints aforementioned, some researchers hold the idea that the effectiveness of homogenous catalysts is actually resulted from heterogeneous mechanism. It is evident that particles formed during combustion will deposit on the surface of piston top and engine wall [11, 18]. Zeller et.al [7] reported that effectiveness of ferrocene on engine emissions does not occur immediately until after 250 hours engine condition. It was also observed that there was no reduction of particulate matters and brake specific NOx emission for a new engine treated with platinum additive until substantial longer periods [12]. These phenomena make it arguable that the homogeneous catalysts may act a heterogeneous role by depositing metal oxide on the piston.

It is likely that all mechanisms are reasonable depending on the types of catalysts and experimental conditions. Diesel combustion has special characteristics which involves both premixed combustion and diffusion combustion. In addition, the fuel/air equivalence ratio differs from location to location and diffusion flame is turbulent. All of these will cause the difference when applying the catalyst in the diesel engines. Different catalysts play different roles in diesel combustion due to the nature of their properties. For example, the picrate is a kind of explosive and will enhance ignition during combusiton while CeO_2 is a kind of oxygen storage chemical. So it is necessary to investigate the mechanism of the working of the homogneous combustion catalysts in diesel combustion process in detail.

4. Proposed Research and Challenges

To the best of our knowledge, the major study of homogeneous combustion catalysts was their effects on engine performance [6, 7, 12]. There are no studies in existence about their mechanisms in diesel combustion. Our present effort aims to investigate the mechanisms of the working of homogeneous catalysts in diesel combustion to confirm their effects on engine efficiency and fuel consumption in diesel engines. By studying the mechanisms of the homogeneous catalysts in diesel combustion through mathematical modelling and experimentation, the results will provide a scientific basis for demonstration and deployment of a new technology. This approach will allow the following challenges to be met.

- Indentify the mechanism of the homogeneous combustion catalysts in diesel combustion process. By performing diesel droplet combustion experiment and mathematical modelling, the mechanism of diesel combustion treated with homogeneous catalysts will be investigated. By comparing diesel combustion process dosed with and without catalysts, the effect of homogeneous combustion catalysts on diesel ignition, flame formation and temperature will be obtained. The experiments to be performed include a cylindrical furnace with temperature controller and colorful CCD camera for temperature measurement, shown in Fig. 2.
- Confirm and quantify the effects of the homogeneous combustion catalysts on fuel consumption and emissions under controlled engine testing conditions systematically. A single cylinder diesel engine coupled to a dynamometer will be used as illustrated in Fig. 3. The measured engine parameters include engine speed, torque, fuel flow rate, combustion pressure, temperature at different locations injector needle lift, intake air flow rate, crankshaft position and exhausts. By using mathematical statistic tool namely Box-Behnken, the fuel consumption and emissions will be measured statistically as a function of the dosing rate of the combustion catalysts, the fuel/air ratio, engine load, engine speed and operating time. This will enable unbiased assessment about the effects of homogeneous catalysts on diesel combustion.
- Study the effect of the catalysts on renewable fuels such as bioethanol and biodiesel. There are limited studies about the effect of the catalysts on renewable fuels. It is evident that the market penetration of alternative fuel like biodiesel is increasing [22]. By investigating the effect of homogeneous combustion catalysts on renewable fuels in diesel engines through experiments shown in Figure. 2 and 3, it is anticipated the results will provide a scientific basis for future development and application of this technology in use of renewable fuels.

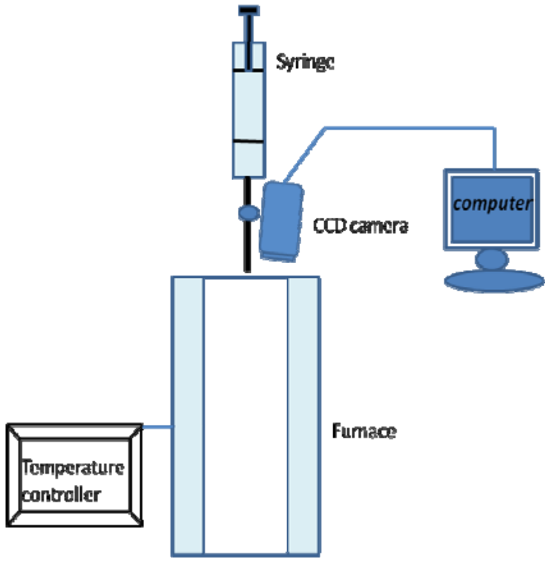

Figure 2 A schematic diagram of diesel droplet combustion system

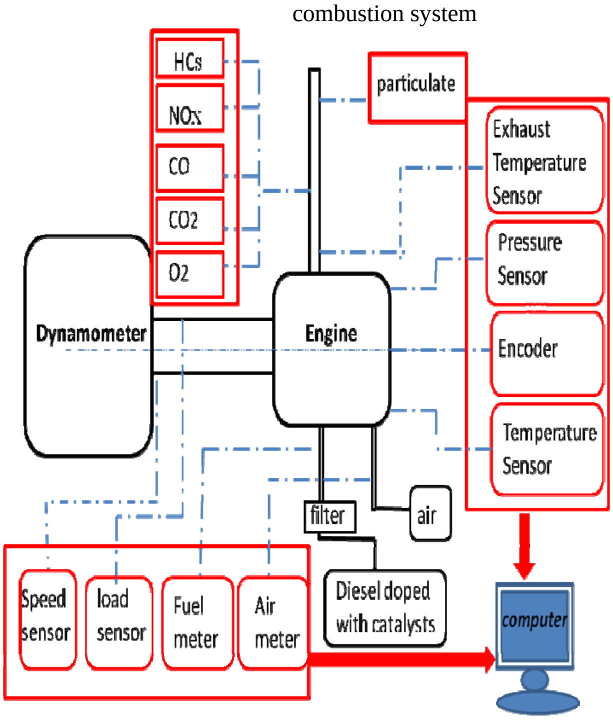

Figure 3 A flow sheet diagram of laboratory controlled engine test system

5. Conclusions

Adding homogeneous combustion catalysts into diesel engine is a promising method in both improving engine efficiency and reducing pollution emission. Our present approach will bring about new understanding of the mechanism of the homogeneous combustion catalysts in diesel engines to provide systematic and scientific basis for application of new Australia technology.

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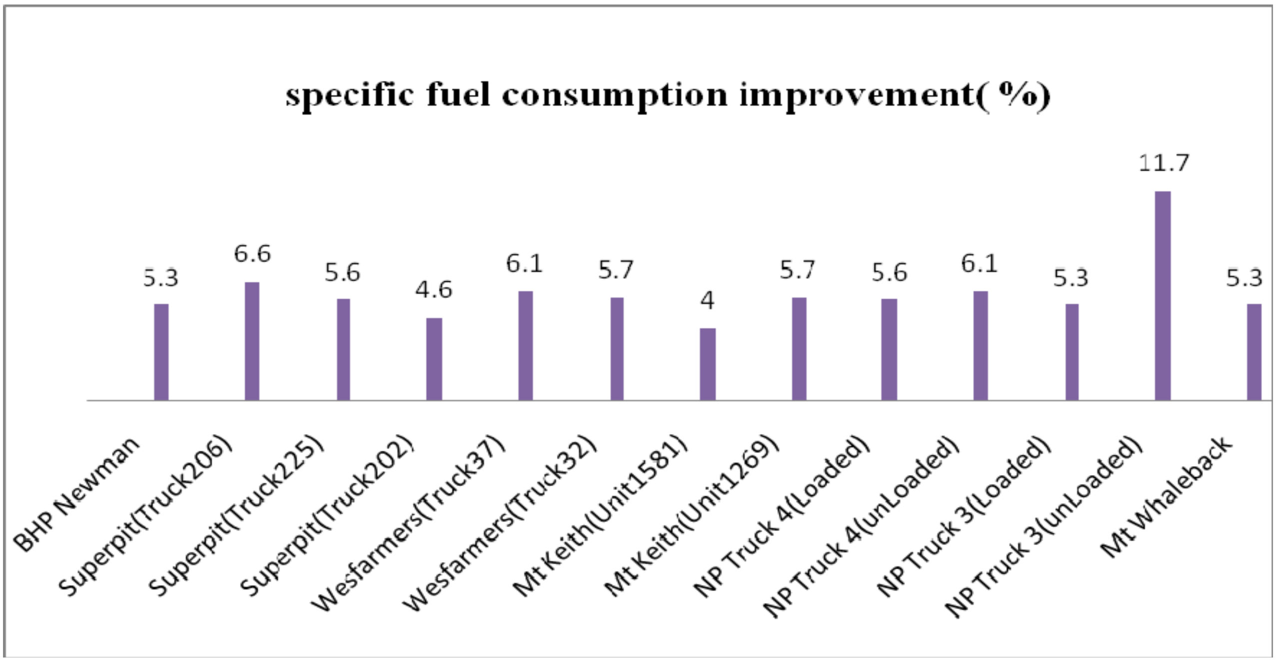

Figure 1 Effect of homogeneous combustion catalysts on specific fuel consumption improvement in diesel engines(NP: Norwich Park mine)