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Metal-Based Additives "Acetylferrocene and Ruthenium Polypyridyl Complex" to Improve Performance and Emission Characteristics of CI Engine

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Metal-based fuel additives have been promising alternative choice to improve diesel engine performance and emission characteristics. Many studies have been performed on use of metal-based fuel additives such as magnesium, platinum, titanium, and cerium in diesel engine. Unlike conventional metal-based additives, Acetylferrocene and Ruthenium polypyridyl complex may be alternative metal-based additives for diesel. This study intends to investigate performance and emission variations of a diesel engine powered by diesel blended with Acetylferrocene and Ruthenium polypyridyl complex additives. In accordance with this purpose, a single cylinder, direct injection diesel engine was used to test these alternative metal additives. Results showed that Acetylferrocene and Ruthenium polypyridyl complex were effective to improve emission characteristics without causing degradation in performance. CO and Soot emissions were showed decrease up to 40% and 32%, respectively, and the fuel consumption characteristic of engine was improved with additives. © 2019 American Institute of Chemical Engineers Environ Prog, 2019

Keywords: metal-based fuel additive, ruthenium polypyridyl complex, diesel engine, exhaust emissions

INTRODUCTION

Diesel engines have widely uses in many sectors such as transport, energy generation, and agriculture since they offer prominent characteristics (low fuel consumption, high durability, reliability, etc.) [1]. It is estimated that diesel engines will have been one of the dominant energy sources in the near future [2]. However, the pollutant emissions emitted from diesel engines cause several environmental and health problems worldwide [3].

Many approaches have been attempted to reduce pollutant emissions from diesel engines without causing any depletion in performance. Modifications of engine, electronic control fuel injection system, exhaust gas recirculation and emission control technologies can be the mains of these approaches. Especially with the advancement in after treatment emission control technologies (diesel oxidation catalysts [DOC], selective catalytic reduction [SCR], diesel particulate filter [DPF], etc.) during last few years, the desired reductions in pollutant emissions has been provided. However, they affect the performance of engine and the high cost of these technologies is an obstacle to use of them [4].

To dope of fuel additive in diesel has been a commercial and effective way to enable effective combustion enhancing chemical and physical properties of fuel [5,6]. Fuel additives advance the efficiency of diesel engines improving fuel consumption and reducing pollutant emissions [7].

Use of fuel additives for diesel engines has been investigated by many researchers during for last decade [8]. To improve engine performance and emission characteristics have been main concern in works. Antioxidants, ignition promoter, corrosion inhibitors, wax dispersant, fuel dyes, antiknock agents, and oxygenates have been fuel additives studied intensely [9]. In addition, metal-based fuel additives such as platinum, cerium, manganese, nickel, cobalt, magnesium, and titanium have been considered as alternative fuel additives in studies [10].

Metal-based additives act as a catalyst in improvement of combustion and reduction of pollutant emissions [11]. High energy level and large surface of metal-based additives generate high catalytic performance in combustion [12]. The metal-based additives produce highly reactive hydroxyl radical in reaction of metals and water vapor in the exhaust emissions. Also, these additives can react directly with carbon atoms in soot. Hereby, the oxidation of soot is enhanced with these reactions [8,13]. The soluble of metal-based additives in diesel without any agglomeration and sedimentation is an impact factor for use in diesel engines [7].

The metal-based additives have been a promising method for researchers to enhance engine performance and reduce pollutant emissions [9]. The results of researches on metal-based additives show that the blends of additives with diesel have significant effect on properties of fuel and combustion characterizes. Lenin *et al.* [14] studied on use of Mn and Cu in diesel engine as nanofuel additive. They found that the use of metal additive improve fuel characteristics and decrease CO, HC, and NO_x emissions significantly. Copper oxides nanoadditives were used with diesel to improve engine performance and emission characteristics by Chandrasekaran *et al.* [15]. In their experimental study, the use of CuO led to increase as 2.19% in brake thermal efficiency while HC, CO, and smoke emissions were significantly reduced. Keskin *et al.* [16] tested

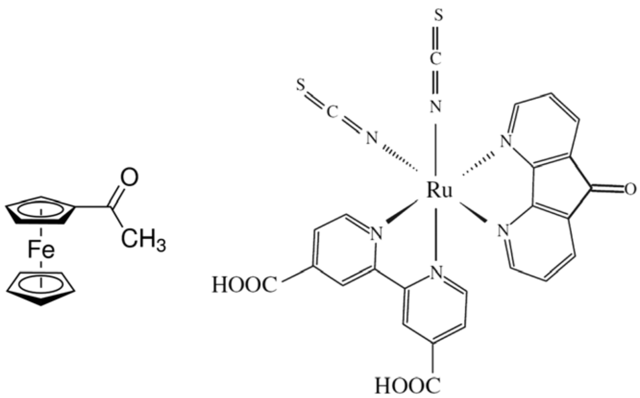

Figure 1. Structure of acetylferrocene and ruthenium polypyridyl complex.

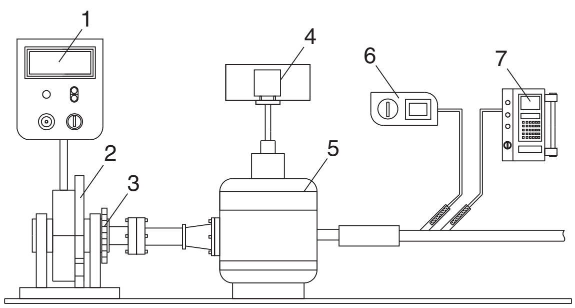

Figure 2. Schematic view of test bench (1: panel, 2: hydraulic dynamometer, 3: magnetic pick-up, 4: fuel tank, 5: engine, 6: sootmeter, 7: gas analyzer).

manganese and magnesium as metal-based additives in diesel engines. Significant decreases in CO and Smoke emissions were obtained in their experimental study. They observed reduction up to 29.82% in smoke with the use of manganese. Srinidhi and Madhusudhan [17] indicated in their study that the use of metal-based additives improve combustion characteristics of diesel engine promoting complete and efficiently combustion of diesel. The CeO_2 effects on performance, combustion and emission characteristics with methyl ester and diesel blends was reported by Karthikeyan *et al.* [18]. Better thermal efficiency, lower fuel consumption and reduction in HC, CO, and NO_x were obtained with the use of CeO_2 nanoparticle additives. Venu and Madhavan [19] used Al_2O_3 nanoparticle with diesel-biodiesel-ethanol-blends. They reported that Al_2O_3 acted as a combustion catalyst and reduced BSFC, NO_x, HC, and CO_2. Rolvin *et al.* [20] used titanium dioxide (TiO_2) as fuel additive in diesel engines. The addition of TiO_2 to diesel improved the specification of neat diesel. They found significant decreases in BSFC, HC, and CO emissions up to 22%, 18%, and 25% respectively. Shaafi and Velraj [21] investigated influence of alumina particles, ethanol and isopropanol blend as additive with diesel-soybean biodiesel. Alumina particles were found effective in improving combustion characteristics and reduction of pollutant emissions. Ryu *et al.* [22] tested oil-soluble Ca- and Fe-based metallic compounds with heavy fuel oil in a large two-stroke marine diesel engine. They confirmed that the use of metallic compounds enhances considerably engine performance and emission characteristics. Kannan *et al.* [23] carried out a study on improvement of diesel engine characteristics with use of $FeCl_3$ as fuel additive. Significant reductions were obtained in CO, HC, and smoke emissions and combustion characteristics of engine were improved

Table 1. Uncertainties in measurements.

Measurements		Uncertainty ±%
Engine speed	rpm	0.11
Torque	Nm	0.27
Brake Power	kW	0.29
BSFC	g/kWh	0.92
CO	(ppm)	2.45
NO_x	(ppm)	2.87
Soot	m^{-1}	2.16

with $FeCl_3$. The effects of TiO_2 nanoparticles addition in diesel/biodiesel/*n*-butanol blends were investigated by Ors *et al.* [24]. They found that TiO_2 nanoparticles did not substantially affected the blends properties. However, the addition of TiO_2 nanoparticles improved the combustion performance. The torque and power of engine increased approximately 10% while BSFC decreased roughly 28%. In addition, emission characteristics were improved by the use of TiO_2 nanoparticles. Jiang *et al.* [25] investigated the thermal properties of carbon coated aluminum and its diesel engine performance. Results showed that carbon coated aluminum is quite conducive to thermal conductivity. BSFC was reduced by up to 13.3% and the emission characteristics were improved with the use carbon coated aluminum.

A wide variety of metal-based additives (Mn, Cu, Ti, Ce, Pt, Ni, Co, etc.) have been studied by many researchers. However, Acetylferrocene and Ruthenium polypyridyl complex have been not investigated exactly as a metal-based additive for diesel yet. This study focuses the use of Acetylferrocene and Ruthenium polypyridyl complex as a metal-based additive in diesel engine. The experimental study is intended to determine the effect of Acetylferrocene and Ruthenium polypyridyl complex on fuel properties and engine characteristics. Actual engine tests were conducted to investigate the influence of Acetylferrocene and Ruthenium polypyridyl complex as metal-based additives on diesel engine performance and emission characteristics.

MATERIAL AND METHODS

Preparation of Blends

Acetylferrocene was purchased from Sigma-Aldrich. Ruthenium polypyridyl complex [Ru^{II}(4,5-diazafluoren-9-one)(4,4′-dicarboxy-2,2′-bipyridyl)-di(thiocyanate)] was synthesized according to previously published method [26]. Structure of these compounds is given in Figure 1.

Acetylferrocene and Ruthenium polypyridyl complex were dopped into diesel as 30 and 50 ppm and, thus, four different blends were prepared for engine tests. Each blend was stirred for 30 min and denoted according to ppm rate of additive in blend as F30, F50, R30, and R50. "D" was used to describe the diesel. All blends and diesel were characterized at Cukurova University Fuel Analysis Laboratory. IKA WERKE Bomb Calorimeter for calorific value, ZX-440 Analyzer for Cetane number, KYOTO DA-130 Portable Digital Density Tester for density, X-ray Sulfur Analyzer for sulfur content, TANAKA Flash Point Tester for flash point, CPP 97–2 Automated Cloud Pour&Cold Filter Plugging Point Analyzer for pour point, Copper Strip Corrosion Tester for copper strip corrosion values, and K 40091 Kinematic Viscosity Meter for viscosity were used in characterization of test fuels. Each specification of test fuels was measured three times and the averages of the measurements were calculated.

Experimental Setup

The schematic view of experimental setup is illustrated in Figure 2. A direct injection, single cylinder, four stroke, air

Table 2. Specifications of test fuels.

	EN 590	D	F30	F50	R30	R50
Calorific value (kJ/kg)	-	44,149	44,102	44,098	44,095	44,016
Density at 15°C (kg/m^3)	820–845	0.830	0.830	0.832	0.829	0.828
Cetane number	Min 51	56.415	56.403	56.398	54.990	54.869
Viscosity at 40°C (cSt)	2.0–4.5	3.3	3.3	3.3	3.2	3.2
Flash Point (°C)	Min 55	55.0	55.0	55.0	54.3	54.3
Sulfur content (mg/kg)	Max 10	7.6	7.6	7.6	7.6	7.6
Pour point (°C)	-	−25	−26	−27	−27	−28
Copper strip corrosion (3 h, 50°C)	1	1	1	1	1	1

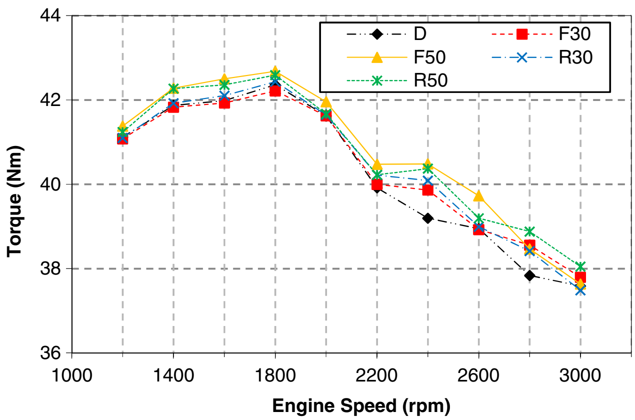

Figure 3. Comparison of torque between diesel and blends with metal-based additives. [Color figure can be viewed at **wileyonlinelibrary.com**]

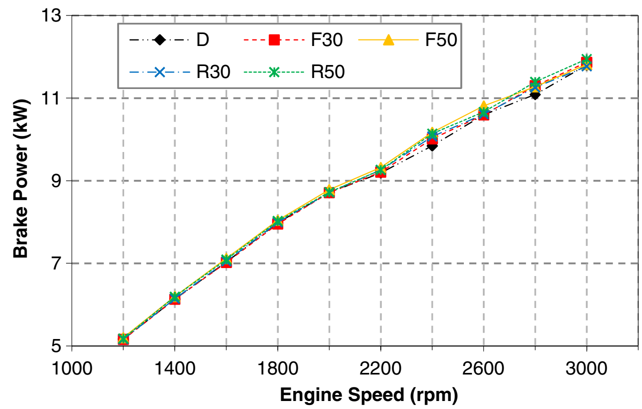

Figure 4. Comparison of power between diesel and blends with metal-based additives. [Color figure can be viewed at **wileyonlinelibrary.com**]

cooled Antor 4 LD 640 diesel engine with a compression ratio 17/1, displacement of 638 cc, 3000 rpm maximum speed, and 10 kW maximum power was used in tests. The engine was mounted to a hydraulic dynamometer, which has up to 1000 Nm measuring torque. A magnetic pickup was used to determine engine speeds while S type load cell measure engine load. The fuel consumption of the engine was measured via a level sensor in the fuel tank of the engine. The value of mass fuel consumption was determined based on the amount of change in fuel level of tank. The ratio of mass fuel consumption to the brake power generated the break specific fuel consumption (BSFC - g/kWh) of engine.

CAPELEC CAP3200 was used to measure Soot (*K* value) with 0–10 1/m measuring range and 0.01 1/m resolution while Testo 350-S had 1 ppm resolution was used to obtain CO and NO_x with 0–10,000 ppm and 0–3000 ppm measuring range respectively. Table 1 shows the uncertainties in measurements.

All tests were conducted at full load conditions and engine speeds from 1200 to 3000 rpm with a constant increment of 200 rpm. Each test was performed with three replicates without any modification in the existing engine and the averages of results were calculated. The same operating conditions were carried out for all tests.

RESULTS AND DISCUSSION

The Specifications of Test Fuels

The chemical and physical properties of blends and diesel are listed in Table 2 comparing with EN590. The specifications of test fuels complied with EN 590 standards in general. Density, sulfur content, copper strip corrosion, and calorific value of blends showed similarity with diesel. Ruthenium polypyridyl complex led to slightly decrease in Cetane number and Flash point compared to diesel. Cetane number of R50 was lower than diesel's as 2.74%. Viscosity of R30 and R50 were measured lower at a rate of 3.03% than diesel's while viscosity of F30 and F50 were same with that of diesel. Compared to diesel, significant decreases in pour point were obtained with blends. Maximum decrease rate for pour point was obtained with R50 as 12%. Similar studies have been shown metal-based additives enhance especially viscosity, flash point, and pour point of fuels [10,27].

Engine Performance Characteristics

Figures 3 and 4 shows torque and brake power, respectively. The torque and power values of blends were showed similarity with diesel. The use of metal-based additives was not led to a significant change in torque and power of test engine. Compared to diesel, maximum increase in torque and power was observed as 3.28% with F50 at 2400 rpm. Maximum torque values were obtained at 1800 rpm for blends and diesel. At this engine speed, the torque of D, F30, F50, R30, and R50 were 42.36 Nm, 42.48 Nm, 42.68 Nm, 42.45 Nm, and 42.59 Nm. In addition, maximum brake power for D, F30, F50, R30, and R50 were measured as 11.80 kW, 11.86 kW, 11.91 kW, 11.82 kW, and 11.89 kW at maximum engine speed (3000 rpm).

Fuel consumption of an engine is an important factor because it is directly linked to vehicle economy. The addition of metal-based additives in diesel engine leads to significant reduction in BSFC [11]. Break specific fuel consumption of diesel and blends at full load condition is given in Figure 5. It can be seen from this figure, BSFC showed a downward trend with the use metal-based additive. Maximum decrease rate was obtained as 5.34% with F50 at 2600 rpm compared to diesel. Averagely F50 led to decrease at a rate of 3.25% in BSFC. While there was not any significant change in calorific value of diesel and blends, the decrease in BSFC can be explained with the catalytic combustion activity of metal-based additives.

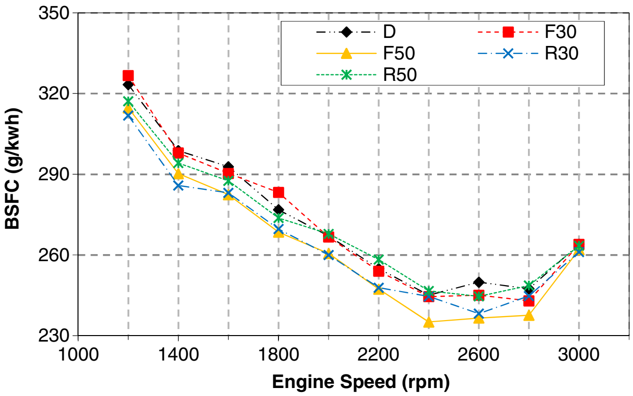

Figure 5. Comparison of break specific fuel consumption between diesel and blends with metal-based additives. [Color figure can be viewed at **wileyonlinelibrary.com**]

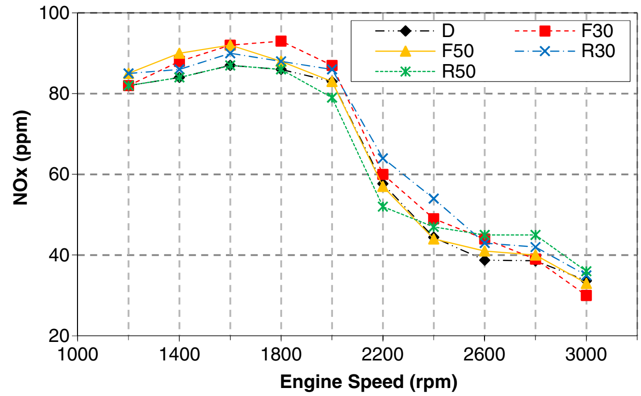

Figure 7. Comparison of NO_x between diesel and blends with metal-based additives. [Color figure can be viewed at **wileyonlinelibrary.com**]

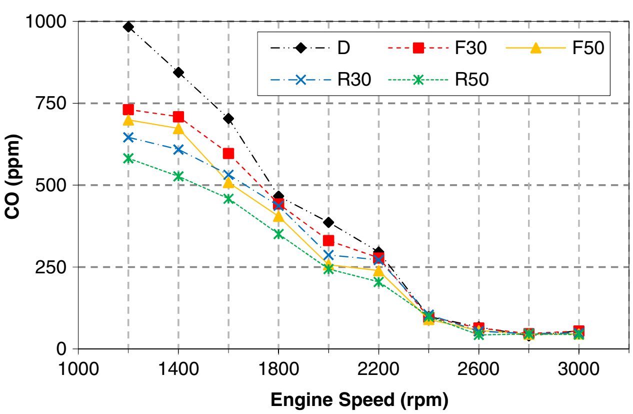

Figure 6. Comparison of CO between diesel and blends with metal-based additives. [Color figure can be viewed at **wileyonlinelibrary.com**]

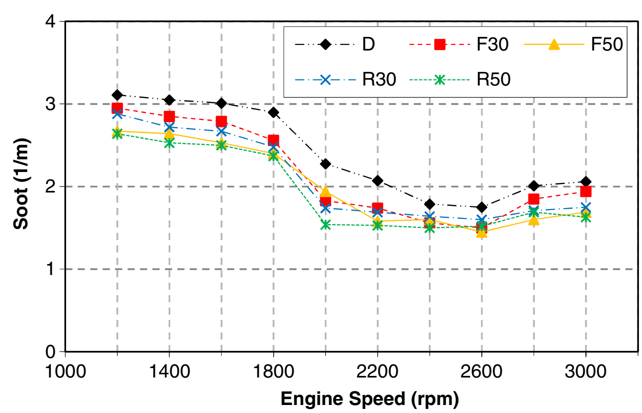

Figure 8. Comparison of Soot between diesel and blends with metal-based additives. [Color figure can be viewed at **wileyonlinelibrary.com**]

Engine Exhausts Emission Characteristics

CO emissions of test fuels are given in Figure 6. The use of metal-based additives led to significant decrease in CO. Maximum decrease was observed as 40.82% with R50 at 1200 rpm compared to diesel. Decreases in CO were obtained averagely 7.31% for F30, 17.40% for F50, 13.52% for R30, and 24.80% for R50. Ruthenium polypyridyl complex showed better performance than Acetylferrocene in CO reduction. For all test fuels, CO emission decreases, as the engine speed increased. Low turbulence rates, chemical kinetic effects, low combustion temperatures, and so forth cause to incomplete combustion, which means high CO emissions. The decreases rates at low engine speeds were found higher than those at higher engine speeds. In high engine speeds (over 2200 rpm), CO emissions values of blends showed similarity with those of diesel. Metal-based additives can be used as a good approach in reduction of high CO emissions at idling speeds. The use of metal-based additives in diesel engine improves the combustion efficiency and temperature. Increase in combustion temperature lead to burn fuel effectively. Similar trends of results were also reported in other studies [4].

Even though the temperature in combustion chamber is a key factor, many parameters such as reaction time of combustion, engine-operating conditions, air-fuel ratio, and so forth plays role in formation NO_x. Figure 7 represents the percentage concentrations of NO_x emission of diesel and blends. In contrast to CO, NO_x emission of blends increased slightly with the use of metal-based additives. Improvement of combustion process by the use of metal-based additives increases NO_x emissions [4]. Compared to diesel, increase rates of F30, F50, R30, and R50 were averagely obtained as 3.92%, 6.15%, 5.72%, and 8.29%. It is estimated that the metal-based additives enhanced the combustion process meaned higher combustion end temperature. The increase in temperature caused a slightly increase in NO_x formation. Maximum NO_x emission value was obtained at 1600 rpm for all test fuels. The increase in engine speed led to decrease in NO_x emissions. Even so, the combustion end temperatures are higher at high engine speeds, decrease in NO_x emissions might be due to low excess air coefficient (λ). These results match with those of other researchers [7,10].

Soot emission emitted from diesel engines is a serious hazard in the atmospheric and can causes serious health problems [28]. The effect of metal-based additives on soot emissions is shown in Figure 8. Considerable improvements in soot emissions were observed with blends. Maximum decrease in Soot emissions was obtained as 32.3% with R50 at 2000 rpm compared to diesel. Compared to Acetylferrocene, Ruthenium polypyridyl complex showed better performance to reduce Soot emissions. The average decreases in Soot emissions for F30, F50, R30, and R50 over the entire range of engine speeds were obtained respectively as 10.71%, 16.52%, 13.27%, and 19.18%. The metal-based additives function as an oxidation catalyst and decrease the oxidation temperature of diesel soot and increase burning of particles [8,29].

The catalyst effect of metal-based additives improves combustion process and release oxidation temperature of fuels [30]. This situation generates reduction in pollutant emissions.

CONCLUSION

This study focused on Acetylferrocene and Ruthenium polypyridyl complex as metal-based additives in diesel engine. Acetylferrocene and Ruthenium polypyridyl complex were blended with diesel and each test fuel was characterized. Actual engine tests were conducted to see the effects of Acetylferrocene and Ruthenium polypyridyl complex on engine performance and emission characteristics. Results showed pour point of diesel decreased up to 12% while other specifications such as density, calorific value, and so forth were similar with diesel. The use of Acetylferrocene and Ruthenium polypyridyl complex led to decrease up to 5.72% in BSFC while there is no significant change in engine torque and power. CO and soot emission showed downward trend while NO_x emission slightly increased. Maximum decreases in CO and Soot emissions were observed respectively as 40.82% and 32.3%. Acetylferrocene and Ruthenium polypyridyl complex functioned as a catalyst and promoted the combustion in diesel engines. Hereby the emission characteristics of diesel engine were improved with the use of these metal-based additives in general. In comparison to Acetylferrocene, Ruthenium polypyridyl complex showed better performance in improvement of emission characteristics of diesel engine.

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