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Using Pd(II) and Ni(II) complexes with *N*,*N*-dimethyl-*N′*-2-chlorobenzoylthiourea ligand as fuel additives in diesel engine

Ali Keskin [a], Kasim Ocakoglu [b,c], İbrahim Aslan Resitoglu [a,*], Gokturk Avsar [d], Fatih Mehmet Emen [e], Barış Buldum [c]

[a] Department of Automotive Engineering, Mersin University, Faculty of Tarsus Technology, TR-33480 Tarsus, Mersin, Turkey
[b] Department of Energy Systems Engineering, Faculty of Tarsus Technology, Mersin University, TR-33480 Tarsus, Mersin, Turkey
[c] Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, TR-33343 Yenisehir, Mersin, Turkey
[d] Department of Chemistry, Mersin University, Faculty of Arts and Science, TR-33343 Mersin, Turkey
[e] Department of Chemistry, Mehmet Akif Ersoy University, Faculty of Arts and Science, TR-15030 Burdur, Turkey

HIGHLIGHTS

- The use of PdL_2 and NiL_2 complexes as fuel additives in diesel engine.
- The effect of metal additives on engine performance and emission.
- Significant decreases in pollutant emissions by using additives.
- Reducing fuel consumption by 7.75% with P100.

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ABSTRACT

Fuel additives have been used to improve engine performance and also to reduce the pollutant emissions that occur after the combustion in engine. The effect of additions of bis-(*N*,*N*-dimethyl-*N′*-2-chlorobenzoylthioureato)palladium (II), PdL_2 and bis-(*N*,*N*-dimethyl-*N′*-2-chlorobenzoylthioureato)nickel (II), NiL_2 complexes into diesel as metal additives was investigated experimentally. PdL_2 and NiL_2 complexes were added as 50 and 100 ppm to diesel and the properties (density, viscosity, calorific value, Cetane number, sulphur content, flash point, pour point and copper strip corrosion) of each test fuel were investigated. In general, the metal additives haven't led to major changes on fuel properties of diesel. However pour point values of additive blends reduced while flash point increased compared to diesel. All blends were tested in a four stroke single cylinder diesel engine to find out the performance and emission characteristic. The results revealed that the use of PdL_2 and NiL_2 complexes nickel has no significant effect on engine torque and brake power while considerable decrease was obtained for engine pollutant emissions (CO, NO_x and smoke). Also the brake specific fuel consumption (BSFC) showed overall declining trend.

1. Introduction

Nowadays, ecological factors have gained importance as economic factors in automotive sector. In addition to the reduction of the prime cost of automotive sector, many studies have been carried out to lower the effect of vehicles on environmental pollution. The most popular fields to get a clean engine releasing less pollutant emissions have been after treatment systems, engine modifications, electronically controlled fuel injection systems and promoting diesel fuel characteristics [1–3]. To use fuel additives in engines is an effective method to improve fuel characteristics, engine performance and reduce pollutant emissions as meeting emission standards (Euro, Tier, etc.) [4,5]. So many fuel additives have been studied as chemical blend with gasoline, diesel, biodiesel, etc. to increase surface area and burn rate of fuels, prevent corrosive effects and improve fuel economy [5–8]. They can be presented typically as oxygenates, antioxidants (stabilizers), antiknock agents, fuel dyes, metal based additives, corrosion inhibitors. The recent studies on using of fuel additives in diesel engine are based especially on improving of biodiesel characteristics and

* Corresponding author at: Mersin University, Faculty of Tarsus Technology, 33500 Mersin, Turkey. Tel.: +90 (0)324 3614 0038; fax: +90 (0)324 361 0043.
E-mail address: aslanresitoglu@mersin.edu.tr (İ.A Resitoglu).

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using as an alternative fuel with diesel blends in diesel engine [9–12]. To promote this aim, especially oxygenate additives containing oxygen in the structure such as esters and alcohols have been extensively used fuel additives in diesel engines [1,13]. Many studies have been investigated on oxygenate additives. These studies demonstrated that oxygenate additives offers a good performance especially on biodiesel to improve its fuel characteristics such as density, viscosity and heating value. Since biodiesel fuel characteristics are varied compared to diesel, fuel additives have been a good choice to equalize the biodiesel characteristic with diesel [13,14].

However the use of metal additives is an alternative choice to improve engine performance and reduce pollutant emissions in diesel engines. Metal additives have catalytic effect on improving combustion process [15]. They have functioned as combustion catalyst to promote the combustion and to reduce fuel consumption with the decrease of pollutant emissions [16,17]. The metal function either reacts with water vapor to produce hydroxyl radicals or directly react with carbon atoms as a catalyst thereby releasing oxidation temperature [15,16]. As a result, remarkable decrease is obtained especially in smoke and CO emissions. To see the effect of metal additives on fuel properties, engine performance and emission characteristics, various metal additives such as titanium, manganese, iron, platinum, barium and cerium were studied in many experimental investigations [16–19]. In these studies, researches have been carried out especially on diesel engine fuelled with blend of biodiesel, diesel and a metal additive. As a result, it showed that metal additives promote the fuel specifications such as viscosity, flash point, pour point, calorific value and Cetane number. Engine performance and emission characteristics are improved significantly.

Benzoyl thioureas are well known class of excellent ligands for transition metals. One of them is *N*,*N*-dialkyl-*N*′-benzoyl thiourea derivatives which form neutral chelates with lots of metal ions in aqueous solutions and these chelates can be extracted with $CHCl_3$ and separated by chromatography [20]. Synthesis and thermal properties of benzoyl thioureas and its metal complexes were studied by researchers [21–29]. Bis-(*N*,*N*-dimethyl-*N*′-2-chlorobenzoylthioureato)palladium (II) and bis-(*N*,*N*-dimethyl-*N*′-2-chlorobenzoylthioureato)nickel (II) complexes were reported in literature [26]. But these complexes haven't been study as diesel additives yet.

This study was conducted to evaluate performance and emission characteristics of an unmodified diesel engine fuelled by bis-(*N*,*N*-dimethyl-N′-2-chlorobenzoylthioureato)palladium (II), PdL_2 and bis-(*N*,*N*-dimethyl-*N*′-2-chlorobenzoylthioureato)nickel (II), NiL_2 complexes as metal additives in diesel. Each additive was doped into diesel fuel as 50 and 100 ppm. The performance and emission tests were carried out at full load and different engine speeds.

2. Material and methods

2.1. Preparation of blends

Bis-(*N*,*N*-dimethyl-*N*′-2-chlorobenzoylthioureato)palladium (II), PdL_2 and bis-(*N*,*N*-dimethyl-*N*′-2-chlorobenzoylthioureato)nickel (II), NiL_2 complexes nickel were synthesized and characterized in our previous study [26]. A solution of 2-chlorobenzoyl chloride (5×10^{-2} mole) in acetone (50 cm^3) was added drop wise to a suspension of potassium thiocyanate (5×10^{-2} mole) in acetone (30 cm^3). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of dimethyl amine (5×10^{-2} mole) in acetone (10 cm^3) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 300 cm^3) was added and the solution was filtered. The solid product was washed with water and purified by recrystallization from ethanol. The metal acetate solutions (2.5×10^{-2} mole) in ethanol (30 cm^3) were added dropwise to the solution of the ligand to secure the ratio of metal:ligand 1:2 with a small excess of ligand in dichloromethane (50 cm^3) at room temperature. The solid complexes were recrystallized from ethanol/dichloromethane mixture (1:1). The PdL_2 and NiL_2 complexes were used as metal additives in this experimental study. To investigate the effect of PdL_2 and NiL_2 additives on engine performance and emission behavior, the each additive was added into diesel as 50 and 100 ppm. The blends of PdL_2 and NiL_2 complexes named P50, P100 and N50, N100 as the additive concentrations in blend, respectively. The diesel named as "D" and thereby five test fuels were generated in total to carry out experimental study.

Characterizations of test fuels were determined at Cukurova University Fuel Analysis Laboratory. To obtain density, viscosity, calorific value, Cetane number, sulphur content, flash point, pour point and copper strip corrosion values of test fuels, respectively KYOTO DA-130 Portable Digital Density Tester (Kyoto Electronics Manufacturing Co., Ltd., Shanghai, China), K 40091 Kinematic Viscosity Meter (Expotech, Houston, TX), IKA WERKE Bomb Calorimeter (IKA-Werke GmbH & Co. KG, Staufen im Breisgau, Germany), ZX-440 Analyzer (ZELTEX, Maryland, USA), X-ray Sulfur Analyzer (Tanaka Scientific Limited, Tokyo, Japan), TANAKA Flash Point Tester (Tanaka Scientific Limited, Tokyo, Japan), CPP 97-2 Automated Cloud, Pour&Cold Filter Plugging Point Analyzer (PAC, Texas, USA) and Copper Strip Corrosion Tester (Koehler Instrument Company, New York) were used.

2.2. Experimental setup

The schematic representation of experimental setup is given in Fig. 1. All test fuels were examined on one cylinder direct injection engine to investigate their effects on engine performance and emissions. Table 1 shows the specifications of test engine. The engine performance and emission tests were conducted under full load condition and different engine speeds. The performance characteristics of diesel engine were evaluated in terms of torque, brake power and BSFC while emission characteristics were evaluated in terms of CO, NO_x and smoke emissions. A hydraulic dynamometer was coupled with test engine to obtain torque and power readings. An S-type load cell situated on dynamometer was used to measure load for torque and power readings while a magnetic pick-up was used to get engine speed values. CO and NO_x emissions were determined using a Testo 350-S gas analyzer

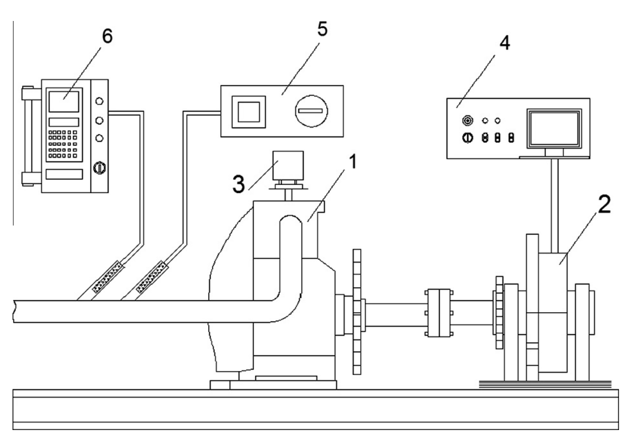

Fig. 1. Schematic diagram of experimental setup (1 – Test engine, 2 – Hydraulic dynamometer, 3 – Fuel tank, 4 – Control panel, 5 – Smoke analyzer, 6 – Diesel emission analyzer).

Table 1
Main characteristics of the test engine.

Manufacturer/type		Antor Diesel 4 LD 640
Cylinders number		1
Swept volume	cc	638
Bore	mm	95
Stroke	mm	90
Compression ratio		17:1
Maximum speed	rpm	3000
Maximum power	HP	13
Maximum brake torque	N m at 1800 rpm	43
Injection type		Direct injection
Cooling system		Air-cooled

Table 2
Specifications of gas analyzers.

Instrumentation		Measuring range	Resolution
CAPELEC CAP3200	*K* value (1/m)	0–10	0.01
Testo 350-S	CO (ppm)	0–10000	1
	NO_x (ppm)	0–3000	1

while CAPELEC CAP3200 analyzer was used to measure smoke emission values (Table 2). All experimental tests were carried out three times and the results were averaged.

3. Results and discussion

3.1. The specifications of test fuels

The changes in diesel properties due to introduction of PdL_2 and NiL_2 additives are shown in Table 3. The derived data were compared with the standard of EN 590. All test fuels are matched with EN 590. Comparing the diesel and metal additives fuels, it is shown that there is not a significant effect of additives on fuel properties in general. The most noticeable change was observed with pour point of test fuels. The use of additives has led to a decrease in 2–5 °C in the pour point according to diesel. The maximum decrease for pour point was obtained with N100 fuel as 5 °C. This decrease leads to the improvement of the cold behavior of the fuel. Flash point properties of metal additive blends showed increase compared to diesel. The maximum flash point value was obtained with N100 as 56.8 °C. The increase of flash point promoted the use and storage of fuel more safely. Except from flash point and pour point, the properties of metal additives were so similar to diesel. In general metal based additives improve pour point, flash point and viscosity [13,17].

3.2. Engine performance results

The variation of torque and brake power of the engine is shown in Figs. 2 and 3 respectively. Additives had no a significant effect on engine torque and power. Since brake power measured at the output shaft is proportional to engine torque and angular velocity (BP = $\omega \cdot \tau$), the rate of change at same angular velocity for brake power and torque showed the same trend. The maximum torque values were obtained at 1800 rpm for all test fuels as 42.36 N m, 42.78 N m, 42.81 N m, 42.78 N m and 42.79 N m for D, P50, P100, N50 and N100 respectively while the maximum brake power of D, P50, P100, N50 and N100 were obtained as 11.8, 11.57, 11.78, 11.51, 11.72 kW at 3000 rpm.

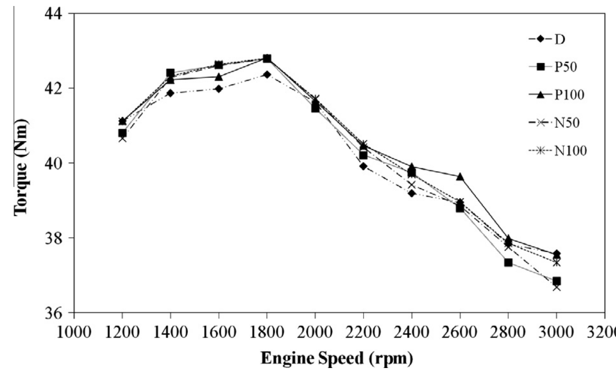

Fig. 2. Torque at different engine speeds and full load condition.

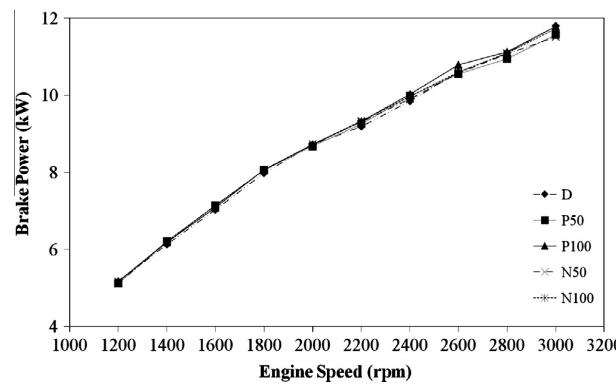

Fig. 3. Brake power at different engine speeds and full load condition.

Fig. 4 shows BSFC of test fuels. It can be seen that using metal additives in diesel fuel lead to decrease in BSFC of engine in general. The decrease of BSFC occurred in direct proportion with the additive content in test fuel. Compared to diesel, the average decrease of BSFC for P50, P100 and N50, N100 was obtained as 1.29%, 3.28% and 1.72%, 3.1% respectively. Maximum decrease in BSFC was obtained with P100 as 7.75% at 1600 rpm. Due to catalyst effect of metal additives, the combustion in engine has been improved and this can lead to the decrease in the BSFC of engine [17]. The decrease in BSFC was also obtained in other studies on uses of metal based additives in diesel or diesel–biodiesel blends

Table 3
Chemical and physical properties of test fuels.

	D	P50	P100	PN50	PN100	EN 590
Density at 15 °C (kg/m^3)	0.830	0.835	0.837	0.832	0.834	820–845
Viscosity at 40 °C (cSt)	3.3	3.3	3.3	3.2	3.2	2.0–4.5
Calorific value (kJ/kg)	44,149	44,164	44,172	44,157	44,165	–
Cetane number	56.415	56.714	56.824	55.987	55.437	Min 51
Sulphur content (mg/kg)	7.6	7.6	7.6	7.6	7.7	Max 10
Flash point (°C)	55	55.6	56.4	56.1	56.8	Min 55
Pour point (°C)	−25	−27	−28	−29	−30	–
Copper strip corrosion (3 h, 50 °C)	1	1	1	1	1	1

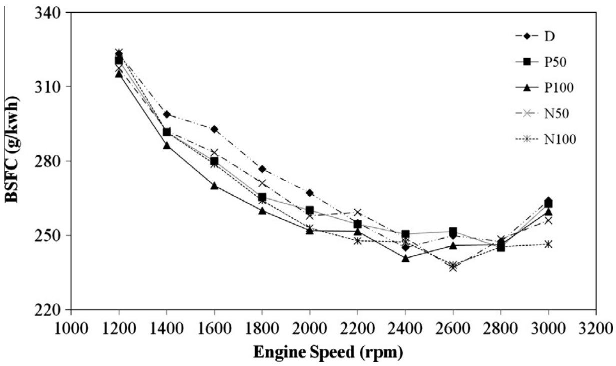

Fig. 4. BSFC at different engine speeds and full load condition.

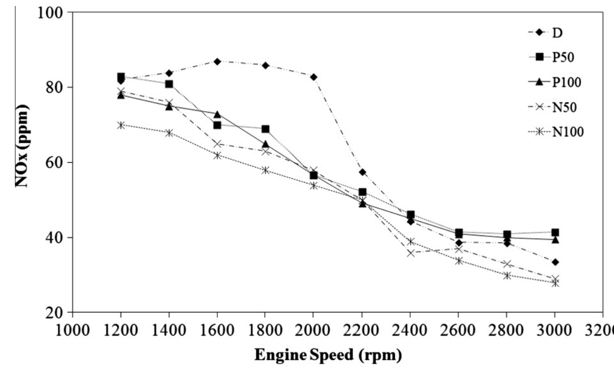

Fig. 6. NO_x emissions at different engine speeds and full load condition.

[16–19,30]. Keskin et al. [17] and Kannan et al. [16] obtained respectively up to 4.16% and 20.1% decrease in BSFC with metal based fuels compared to non metal based fuel.

3.3. Engine exhausts emission results

Although significant changes on engine performance were not obtained with additive blends, the pollutant emissions values showed significant decrease in CO, NO_x and smoke emissions up to 68.15%, 34.93% and 50.24% respectively.

CO is a colorless, odorless and poisonous gas that is produced as a result of incomplete combustion of air–fuel mixture, low combustion cycle time in the engine or lower temperature of the combustion chamber [31]. The effect of metal additives on CO emission is shown in Fig. 5. It can be seen that CO emission of metal additives was found to lower than the ones from diesel. The CO emissions were the highest at lower engine speed for all test fuels. It is observed that average decreases in the CO emissions of N50, N100, P50 and P100 were 32.65%, 42.56%, 44.53% and 50.24% respectively at all engine speeds.

Due to higher combustion temperature; NO_x, which is an important precursor to acid rain has the highest proportion of pollutant emissions in diesel engines [2]. Fig. 6 shows NO_x emission of the engine. As CO emissions, NO_x emissions of test fuels showed downward trend in general. The experimental results of NO_x emission for all additive fuels were obtained lower compared with diesel results. Maximum decrease of NO_x emission was obtained with N100 as 34.93% at 2000 rpm. Compared PdL_2 and NiL_2 complexes, NiL_2 showed a better performance to reduce NO_x emissions. The average reductions in NO_x emissions for P50, P100, N50 and N100 over the entire range of engine speeds were respectively 4.17%, 7.43%, 16.04% and 20.67% compared to diesel. The lowest value of NO_x emission was obtained as 28 ppm with N100 at 3000 rpm.

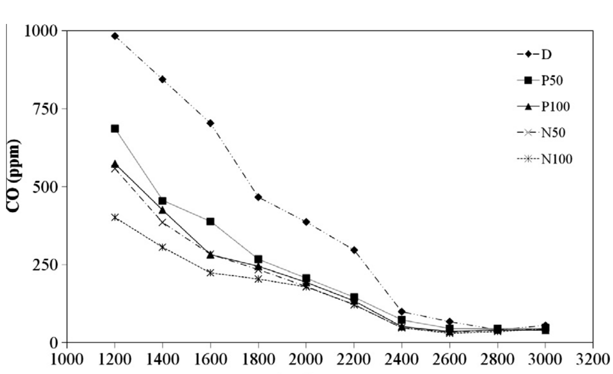

Fig. 5. CO emissions at different engine speeds and full load condition.

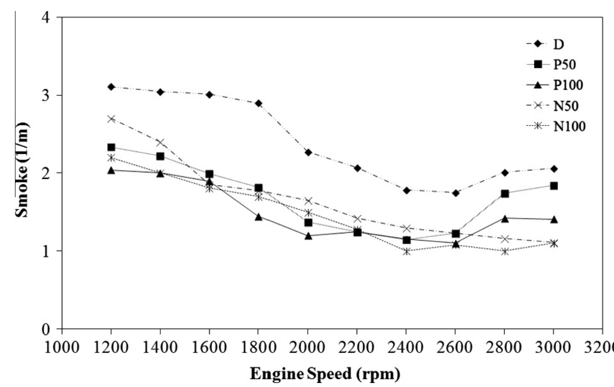

Fig. 7. Smoke level at different engine speeds and full load condition.

The smoke emission of test fuels is shown in Fig. 7. Different from CO and NO_x emissions, smoke emission was showed significant decrease not only at low engine speed but also all engine speeds in comparison to diesel. The smoke emission curves for all additive fuel were lower than that of diesel. Compared to diesel, the smoke emissions decreased averagely 29.01%, 37.63%, 31.6%, 39.64% with P50, P100, N50 and N100 respectively over the entire range of engine speeds.

Although so many parameters such as fuel properties, engine type, engine operating condition, air–fuel ratio, injection timing, compression ratio and injection pressure affect the pollutant emission released from diesel engine, the base point of pollutant emissions is the combustion. The overall improving effects of the innovated metal additives on engine emission characteristics (CO, NO_x and smoke) could be attributed to the fact that metal additives improve combustion process as a catalyst and thereby releasing oxidation temperature of fuels [13,16]. The same effects were seen in other studies for engine emission characteristics [16–19,30]. Kannan et al. [16] obtained a decrease by 52.6%, 26.6% and 6.9% respectively in carbon monoxide (CO), total hydrocarbon (THC) and smoke emission while Keskin et al. [17] obtained a decrease by 16.35% and 29.82% in CO emission and smoke opacity respectively.

4. Conclusion

In this study, it is aimed to see the effect of PdL_2 and NiL_2 complexes on fuel properties, engine performance and emission. The properties of metal additives doped with diesel were presented. Performance and emission evaluations of test fuels were conducted on a single cylinder, four stroke, direct injection and air cooled engine. In conclusion, it is shown that adding PdL_2 and NiL_2 complexes in diesel fuel has caused no significant change on the fuel properties. However the metal additives reduced pour point and raised the flash point of diesel. The performance of engine showed similar results in both diesel and metal additive fuels in general while BSFC decreased up to 7.75%. Furthermore using PdL_2 and NiL_2 complexes as fuel additives in diesel engine presented significant decreases in pollutant emissions (CO, NO_x, and smoke). Compared to PdL_2 and NiL_2 complexes, NiL_2 has the stronger effect on reducing pollutant emission. Maximum reduction in CO, NO_x and smoke emission were obtained with N100.

References

[1] Kadarohman A, Hernani K, Rohman I, Kusrini R, Astuti RM. Combustion characteristics of diesel fuel on one cylinder diesel engine using clove oil, eugenol, and eugenyl acetate as fuel bio-additives. Fuel 2012;98:73–9.

[2] Reşitoğlu İA, Altınışık K, Keskin A. The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. Clean Tech Environ Policy 2015;17:15–27.

[3] Barrios CC, Martín C, Domínguez-Sáez A, Álvarez P, Pujadas M, Casanova J. Effects of the addition of oxygenated fuels as additives on combustion characteristics and particle number and size distribution emissions of a TDI diesel engine. Fuel 2014;132:93–100.

[4] Tsanaktsidis CG, Favvas EP, Scaltsoyiannes AA, Christidis SG, Katsidi EX, Scaltsoyiannes AV. Natural resins and their application in antifouling fuel technology Part I: improving the physicochemical properties of diesel fuel using natural resin polymer as a removable additive. Fuel Process Technol 2013;114:135–43.

[5] İleri E, Koçar G. Effects of antioxidant additives on engine performance and exhaust emissions of a diesel engine fueled with canola oil methyl ester–diesel blend. Energy Convers Manage 2013;76:145–54.

[6] Ashraful AM, Masjuki HH, Kalam MA, Rashedul HK, Sajjad H, Abedin MJ. Influence of anti-corrosion additive on the performance, emission and engine component wear characteristics of an IDI diesel engine fueled with palm biodiesel. Energy Convers Manage 2014;87:48–57.

[7] Roy MM, Wang W, Alawi M. Performance and emissions of a diesel engine fueled by biodiesel–diesel, biodiesel–diesel-additive and kerosene–biodiesel blends. Energy Convers Manage 2014;84:164–73.

[8] Vedharaj S, Vallinayagam R, Yang WM, Chou SK, Lee PS. Effect of adding 1,4-Dioxane with kapok biodiesel on the characteristics of a diesel engine. Appl Energy 2014;136:1166–73.

[9] Beck A, Pölczmann G, Eller Z, Hancsok J. Investigation of the effect of detergent-dispersant additives on the oxidation stability of biodiesel, diesel fuel and their blends. Biomass Bioenergy 2014;66:328–36.

[10] Vallinayagam R, Vedharaj S, Yang WM, Saravanan CG, Lee PS, Chua KJE, et al. Impact of ignition promoting additives on the characteristics of a diesel engine powered by pine oil–diesel blend. Fuel 2014;117:278–85.

[11] İleri E, Koçar G. Experimental investigation of the effect of antioxidant additives on NO_x emissions of a diesel engine using biodiesel. Fuel 2014;125:44–9.

[12] Tosun E, Yilmaz AC, Ozcanli M, Aydin K. Determination of effects of various alcohol additions into peanut methyl ester on performance and emission characteristics of a compression ignition engine. Fuel 2014;126:38–43.

[13] Rashedul HK, Masjuki HH, Kalam MA, Ashraful AM, Ashrafur Rahman SM, Shahir SA. The effect of additives on properties, performance and emission of biodiesel fuelled compression ignition engine. Energy Convers Manage 2014;88:348–64.

[14] Broatch A, Tormos B, Olmeda P, Novella R. Impact of biodiesel fuel on cold starting of automotive direct injection diesel engines. Energy 2014;73:653–60.

[15] Lenin MA, Swaminathan MR, Kumaresan G. Performance and emission characteristics of a DI diesel engine with a nanofuel additive. Fuel 2013;109:362–5.

[16] Kannan GR, Karvembu R, Anand R. Effect of metal based additive on performance emission and combustion characteristics of diesel engine fuelled with biodiesel. Appl Energy 2011;88:3694–703.

[17] Keskin A, Gürü M, Altıparmak D. Influence of metallic based fuel additives on performance and exhaust emissions of diesel engine. Energy Convers Manage 2011;52:60–5.

[18] Gürü M, Artukoğlu BD, Keskin A, Koca A. Biodiesel production from waste animal fat and improvement of its characteristics by synthesized nickel and magnesium additive. Energy Convers Manage 2009;50:498–502.

[19] Keskin A, Gürü M, Altıparmak D. Biodiesel production from tall oil with synthesized Mn and Ni based additives: effects of the additives on fuel consumption and emissions. Fuel 2007;86:1139–43.

[20] Konig KH, Schuster M, Steinbrech B, Schneeweis G, Schlodder R. N,N-dialkyl-N0-benzoylthioharnstoffe als selective extractionsmittel zur abtrennung und anreicherung von platinmetallen. Fresen Z Anal Chem 1985;321:457–60.

[21] Yeşilkaynak T, Binzet G, Emen FM, Flörke U, Külcü N, Arslan H. Theoretical and experimental studies on N-methylpyridin-Yl-carbamothioyl)biphenyl carboxamide. Eur J Chem 2010;1(1):2–6.

[22] Binzet G, Emen FM, Florke U, Yesilkaynak T, Kulcu N, Arslan H. 4-chloro-N-[N-(6-methyl-2-pyridyl)carbamothioyl]benzamide. Acta Cryst 2009;E65:O81–2.

[23] Arslan H, Emen FM, Külcü N. Structure and vibrational spectra of N,N-dimethyl-N′(2-chlorobenzoyl)thiourea: Hartree-Fock and density functional theory studıes. Asian J Chem 2007;19(3):1888–96.

[24] Emen FM, Flörke U, Külcü N, Arslan H. N-(3,5-dinitrobenzoyl)-N-N-diethylthiourea. Acta Cryst 2006;E62:O3814–5.

[25] Arslan H, Flörke U, Külcü N, Emen FM. Crystal structure and thermal behaviour of copper(II) and zinc(II) complexes with N-pyrrolidine-N′-(2-chlorobenzoyl) thiourea. J Coord Chem 2006;59(2):223–8.

[26] Emen FM, Arslan H, Külcü N, Flörke U, Duran N. Synthesis, characterization and antimicrobial activities of some metal complexes with N′-(2-chlorobenzoyl)thiourea ligands: the crystal structure of fac-[CoL3] and cis-[PdL2]. Pol J Chem 2005;79:1615–26.

[27] Emen FM, Flörke U, Külcü N, Arslan H. Cis-Bis(N,N-dimethyl-N-2-chlorobenzoyl thioureato) nickel(II). Acta Cryst 2003;E59:m582–3.

[28] Arslan H, Vanderveer D, Emen F, Külcü N. Crystal Structure of cis-bis(N,N-dimethyl-N′-4-chlorobenzoylthioureato)palladium(II), Pd(C10H10ClN2OS)2. Z Kristallogr NCS 2003;218:479–80.

[29] Emen FM, Flörke U, Külcü N, Arslan H. (N-2-chlorobenzoyl)-N-(pyrrolidin-1-yl) thiourea. Acta Cryst 2003;E59:o1159–60.

[30] Keskin A, Gürü M, Altıparmak D. Biodiesel production from tall oil with synthesized Mn and Ni based additives: effects of the additives on fuel consumption and emissions. Fuel 2007;86:1139–43.

[31] Mirzajanzadeh M, Tabatabaei M, Ardjmand M, Rashidi A, Ghobadian B, Barkhi M, et al. A novel soluble nano-catalysts in diesel–biodiesel fuel blends to improve diesel engines performance and reduce exhaust emissions. Fuel 2015;139:374–82.