

Experimental Research of the Effects of Benzoylthiourea Derivative Fuel and Gasoline Mixtures on Engine Performance and Emissions

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Abstract

In this study, the influences of Benzoylthiourea Derivative Fuel N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide as an additive into gasoline were researched on engine performance and exhaust emissions. For this purpose, a single-cylinder four stroke gasoline engine was run at wide open throttle, and 2400, 2800, 3200, 3600 and 4000 rpm engine speeds. The change of engine torque, power output, specific fuel consumption, thermal efficiency, CO, CO₂ and HC emissions were experimentally investigated. The maximum engine torque at 2800 rpm for the TF-1 fuel was increased by 9.60% compared to gasoline. It has been found that the maximum effective power is decreased, by about 5.3% and 1.26% using TF-1 and TF-2 compared to pure gasoline respectively. Thermal efficiency increased by nearly 25% and 7% for TF-1 and TF-2 test fuels at 2800 rpm compared against pure gasoline respectively. CO and HC reduced with benzoylthiourea derivative fuel addition compared to gasoline. Test results showed that benzoylthiourea derivative fuel additive N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide showed good performance as an additive in a spark ignition engine.

Keywords: Benzoylthiourea, Gasoline, Exhaust Emissions, Engine Performance, Internal Combustion Engine

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1. Introduction

Technological development is mainly impacted by the usage of energy resources. In particular, in the automotive industry, fossil fuels play a crucial role in meeting the energy demand. Nevertheless, these fuels lead to rapid and permanent pollution of the atmosphere, water, and soil. Additionally, petroleum, the raw material for fossil fuels, is quickly depleting. Scientists and experts are exploring high-efficiency alternative combustion modes, alternative fuels with reduced emissions [1].

Compression ignition diesel engines emit (release) high levels of pollutants such as NO_x, soot, CO, and UHC which pose severe health and environmental risks. Most of these emissions can lead to water and air pollution, reducing visibility, and causing global climate change. In order to overcome this challenge, many researchers have started to investigate alternative resource. Fuel additives are substances that can be utilized into fuel to modify its properties and improve results without significant variations to the current engine technology. They are useful and effective in improving fuel properties [2-7]. Besides, different methods have been tried to reduce both fuel consumption and emissions, such as improving the clutch pedal distance, and electromobility-charging systems in electrical vehicles [8,9].

Numerous studies have been conducted on different fuel additives in diesel and gasoline engines recently. These studies aimed at improving combustion and engine performance by using high oxygen-content fuel additives. Some of the chemicals subject to research on these additives are benzoylthiourea and its derivatives. Thioureas have highly effective biological applications and are known as versatile chemicals as well [10]. Structures containing C, N, S atoms in their chemical composition and represented by the general formula CSN₂H₄ are called thioureas. In thiourea derivative ligands and metal complexes, many new structures can be obtained depending on the changing substituted groups and metals [11,12]. Thiourea derivatives are of interest in the field of pharmaceutical chemistry. Benzoylthiourea derivatives also provide numerous binding opportunities to transition metal ions. In this context, various transition metal complexes with different coordination modes of benzoylthiourea derivatives including platinum, rhodium, palladium, copper, nickel, and zinc have been considered in many studies [13-16]. Besides, synthesized compounds derived from benzoylthiourea are also used in various antibacterial and biological applications [17,18].

Other studies on benzoylthiourea derivatives are investigated as fuel additives. Benzoylthiourea derivatives can be utilized as fuel additives to improve fuel properties in internal combustion engines.

In addition, the use of benzoylthiourea derivative compounds tends to improve performance and decrease emissions. However, there is a limited number of studies in the literature on benzoylthiourea and its derivatives as fuel blends. Some research articles on benzoylthiourea and its derivatives are presented in this study.

Gumus et al. [19] conducted a study to synthesize N-(diethyl-carbamothioyl)-4-fluorobenzamideligand and its Pt(II) complex. They revealed that the compound's structure was in line with that of other derivatives of thiourea. Solmaz et al. [20] used Benzoylthiourea-palladium(II) complexes as catalysts in the Suzuki C–C coupling processes. They discovered that these ligand complexes had a very modest catalyst loading and were highly active for the production of biaryl units. Solmaz and Arslan [21] focused on the synthesis of two new Pd^{II} complexes based on a 4-fluoro substituted benzoylthiourea ligand and its elemental analysis. They assessed the Pd II complexes' catalytic activity using the Suzuki-Miyaura cross-coupling process. Khan et al. [22] focused on transition metal complexes and thiourea derivatives. They synthesized a benzoylthiourea derivative (L) and its gold(I), copper(I), silver(I) and complexes. After this process, Ligand L and its complexes were analyzed using UV/visible, FT-IR, ¹H- and ¹³C NMR spectroscopy. The complexes were evaluated for their cytotoxic, antifungal, antioxidant, and DNA-binding properties. Limbeck et al. [23] investigated the emission factors for Platinum and Palladium in PM_{2.5}, PM₁₀, and total suspended particulates that are segregated based on size. Palladium was examined via a flow injection approach with ETAAS detection to determine Pd content in environmental samples. The emission factors for Pt and Pd from on-road vehicles were measured both in total and based on size segregation. Their study showed that the emission factors for Pt and Pd from on-road vehicles were measured both in total and based on size segregation in the Kaisermuhlen Tunnel in Vienna, Austria. Inside the tunnel, the highest levels of Pt and Pd concentrations have been found in total suspended particulate matter samples, and the concentration was reduced in the size-segregated PM₁₀ and PM_{2.5} samples.

Keskin et al. [24] performed a research to see the influence of adding bis-(N, N-dimethyl-N'-2-chlorobenzoylthioureato) palladium (II), PdL₂ and bis-(N, N-dimethyl-N'-2-chlorobenzoylthioureato) nickel (II), NiL₂ complexes as metal additives to diesel. The study presented that the addition of PdL₂ and NiL₂ complexes to diesel fuel did not cause any significant change in fuel properties. Nevertheless, the metal additives decreased the pour point and increased the flash point of diesel fuel. Engine performance was generally similar for both diesel and metal-added fuels, while BSFC decreased by about 7.75%. Moreover, PdL₂ and NiL₂ complexes in compression ignition engine showed 68.15%, 34.93% and 50.24% reduction in pollutant emissions for CO, NO_x and smoke, respectively. In another study, Keskin et al. [25] investigated the influence of diesel-biodiesel mixtures containing palladium-based and acetylferrocene additives on performance and emissions in another study. Bis-(N, N-dimethyl-N'-2-chlorobenzoylthioureato) palladium (II), PdL₂, was prepared as a palladium-based additive by using the additives at a dosage of 25 ppm in the blended fuels. The effects of these additives on emission, performance, and vibration were investigated. Viscosity, density and pour point of blended

fuels raised, but the cetane number and the calorific value declined. There was no significant influence on cylinder pressure in case metal-based additives were used. PM and CO were reduced up to 60.07% and 51.33%, respectively.

Yeşilkaynak et al. [26] synthesized and characterized N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide (C₁₃H₉BrClN₃OS). In the current study, N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide (C₁₃H₉BrClN₃OS) was investigated for the first time as a gasoline additive. N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamidedissolved in dichloromethane and soluble in gasoline was prepared, and tested in an engine test bed with a single-cylinder gasoline engine. To research the influences of benzoylthiourea derivative compounds used as fuel additives on performance and emissions, a test engine was operated at 2400, 2800, 3200, 3600 and 4000 rpm at full load. Previously untested fuel additive was mixed with gasoline at different ratios (0.5 mL and 1.5 mL) and its effects on engine torque, effective power, SFC, thermal efficiency, CO, CO₂, and HC emissions were experimentally investigated.

2. Material and Method

The experimental study was conducted at Burdur Mehmet Akif Ersoy University High Vocational School of Technical Sciences Automotive Technology Laboratory. A single-cylinder spark ignition engine was utilized to investigate the influences of the synthesized fuel additive on performance and emissions (CO, CO₂, and HC). A schematic view of the test setup is given in Figure 1. The technical specifications of the test engine are shown in Table 1.

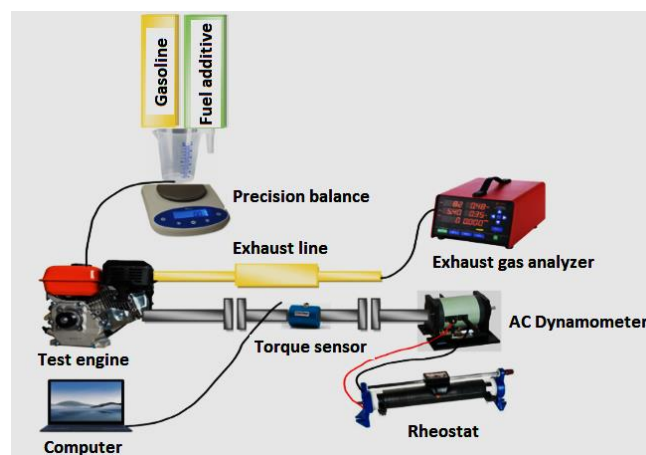


Fig.1. Schematic view of the engine setup

Table 1. The technical specifications of the test engine

Model	Honda GX160
Bore x strok [mm]	68x45
Cylinder volume [cm ³]	163
Compression ratio	8.5:1
Maximum power output HP@3600 rpm	5.5
Maximum Torque [Nm]@2500 rpm	10.78
Cooling system	Air-cooled

Obtaining precise data and reducing experimental errors are vital in experimental studies. Therefore, the measurements were carried out after the test engine reached operating temperature at stable operating conditions. Benzoylthiourea derivative additive was added to pure gasoline to investigate the performance and emissions. The test engine was operated at 2400, 2800, 3200, 3600, and 4000 rpm at full throttle opening. The test fuel mixtures were obtained by adding 0.5 mL and 1.5 mL of additives to pure gasoline. Pure gasoline was used as a reference in the study. The blend ratios and properties of the test fuel utilized in the experimental research are given in Table 2 and Table 3, respectively.

Table 2. Test fuels and mixing ratios

Fuels	Mixing ratios
Gasoline	100 % Gasoline (500 mL)
TF-1 (0.5 mL)	0.5 mL + 100% Gasoline
TF-2 (1.5 mL)	1.5 mL + 100% Gasoline

Table 3. Properties of test fuels [27,28]

Properties	Gasoline
Density [kg/m ³]	746
Latent heat of vaporization[kJ/kg]	331.6
Flash point [°C]	-43
Auto ignition temperature [°C]	257.2
Boiling point [°C]	30-225
Octane number	96.47

Figure 2 shows the chemical structure of the Benzoylthiourea derivative fuel additive N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide used in the experiments [26].

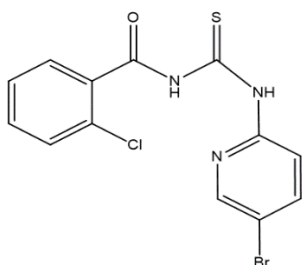


Fig. 2. Chemical structure of benzoylthiourea derivative fuel additive N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide

Table 4 shows some properties of the fuel additive.

Table 4. Some properties of the fuel additive [26]

Properties	N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide
Chemical formula	C ₁₃ H ₉ BrClN ₃ OS
Elemental analysis	C:41.6, H:2.6, N:11.5, S:8.8

The test engine was connected to an AC dynamometer to acquire the full load speed characteristics of the spark ignition engine, as depicted in Fig. 1. The test engine running at full open throttle was loaded and tested at different speeds by stepwise operation of the circuit elements (resistors) connected to the dynamometer output. PLT Power

precision scale (0.5 g) was used to determine the fuel consumption during test. Burster 8661 model torque sensor was mounted between the AC dynamometer and the engine to observe torque and engine speed data. Obtained data during the test were transmitted to the computer via a cable connection. These data were continuously monitored and recorded via Digivision interface. Technical properties of the torque sensor are listed in Table 5.

Table 5. Technical properties of the torque sensor

Model	Burster 8661
Nominal torque output voltage [V]	+10
Insulation resistance [MΩ]	>5
-3 dB cutoff frequency [Hz]	200
Fluctuation [mV]	<50
Driver signal (K pin) [V DC]	10...30

CO, CO₂, and HC emissions were determined with a gas analyzer (SUN MGA1500). Technical properties of the device are listed in Table 6.

Table 6. Technical properties of the exhaust gas analyzer

	Operating range	Accuracy
CO	0-14 %	0.001 %
HC	0-9999 ppm	1 ppm
CO ₂	0-18 %	0.1 %
NO _X	0-5000 ppm	1 ppm
λ	0-4	0.001 %
O ₂	0-25 %	0.01 %

Uncertainty analysis was determined by Eq. (1) [29-33].

$$\Delta f = \left[\left(\left(\frac{\partial f}{\partial x_1} \right) \Delta x_1 \right)^2 + \left(\left(\frac{\partial f}{\partial x_2} \right) \Delta x_2 \right)^2 + \dots + \left(\left(\frac{\partial f}{\partial x_n} \right) \Delta x_n \right)^2 \right]^{1/2} \quad (1)$$

Table 7. Uncertainty analysis results

	Accuracy	[%] Uncertainty
Fuel consumption [g]	± 0.5	± 0.16
Torque [Nm]	± 0.01	± 0.38
Power [kW]	± 0.01	± 0.13

3. Results and Discussion

Test fuel mixtures were prepared by adding 0.5 mL and 1.5 mL of a fuel additive with the chemical composition (C₁₃H₉BrClN₃OS) into pure gasoline after the test engine was running steadily in the experimental setup. Engine torque values for the fuels are presented in Figure 3. The highest torque was obtained at 2800 rpm for all test fuels. The engine torque raised using fuel additive (TF-2). However, the engine torque declined using additive (TF-1). The highest torque at 2800 rpm for the TF-1 fuel was increased by 9.60% compared to gasoline. However, the maximum torque was only increased by 0.38% which has a slight effect on gasoline. In addition to this, as the engine speed increases, the gas leakage and thermal losses increase for each stroke. Thus, the engine torque de-

creases for all test fuels with the rise of engine speed. The variations of torque compared to engine speed is given in Figure 3.

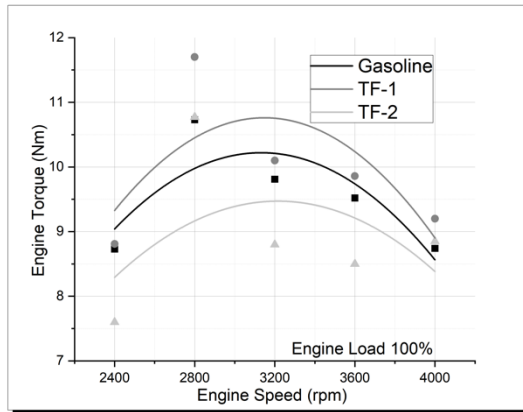


Fig. 3. The variations of engine torque

Figure 4 depicts the variations of engine power output with engine speed. The power output depending on the engine speed raises with all test fuels. The highest engine power output was calculated at 4000 rpm for TF-1. It is seen that the maximum effective power is decreased, by about 5.3% and 1.26% using TF-1 and TF-2 compared to pure gasoline respectively. When fuel additives are added (TF-2), engine power generally reduces compared to pure gasoline. The work done per unit of time raises with the increased engine speed. The homogeneity of the mixture raises with engine speed which is better mixing of the fuel and air molecules. Besides, possible oxidation reactions occurring throughout the combustion chamber increase.

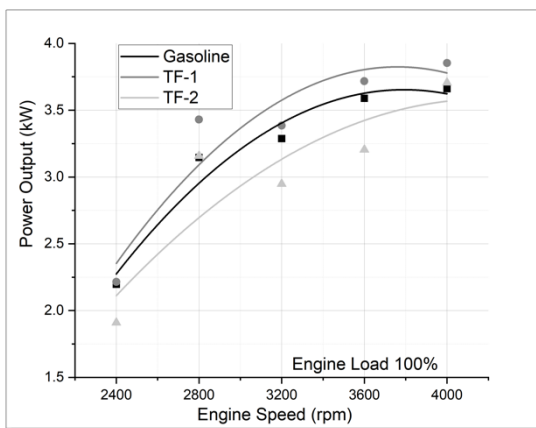


Fig. 4. The variation of power output for different test fuels

Figure 5 denotes the effects of different test fuels on specific fuel consumption (SFC) varying engine speeds. Specific fuel consumption is a very significant parameter for internal combustion engines and should be defined as the amount of fuel consumed by a vehicle for each unit of power output. The effective power decreases due to mechanical losses and lack of oxygen which is required for complete combustion and increases at low and high engine speeds.

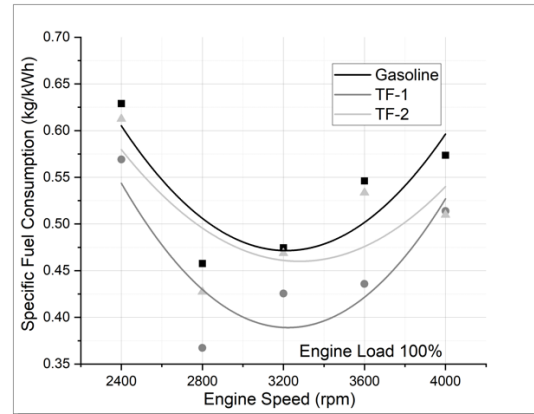


Fig. 5. The influences of test fuels on SFC

It was observed that SFC decreased with the addition of fuel additives (TF-1). However, the SFC increased with TF-2 compared to TF-1. As the amount of additive raises in the fuel blend, the fuel consumed per unit of power increases. The maximum SFC was computed based on reference fuel which is pure gasoline. The minimum SFC values for the test fuels were obtained at 2800 rpm. The lowest SFC was determined with TF-1. SFC decreased by approximately 19.8% and 6.6% for TF-1 and TF-2 according to gasoline at 2800 rpm respectively. The results presented in Figure 5 indicate that the usage of additives has a good effect on SFC.

Figure 6 represents the influence of different test fuels on thermal efficiency at various engine speeds. Thermal efficiency is the conversion of heat energy obtained from the fuel into net work. It is a significant performance variable that is widely used in internal combustion engines. Low engine speeds allow for adequate time for heat transfer. This can lead to a decrease in the average gas temperature inside the cylinder which results in reduced efficiency. Likewise, high engine speeds reduce volumetric efficiency due to gas leakage and flow losses. Insufficient oxygen during combustion results in incomplete burning and the retention of unburned hydrocarbons in the combustion chamber. The remaining fuel molecules are then expelled from the cylinder. Oxidation reactions slow down due to oxygen deficiencies, leading to a decline in thermal efficiency at high engine speeds [34]. Maximum thermal efficiency was reached at 2800 rpm, where the SFC values were at their minimum. Maximum thermal efficiency was observed at 2800 rpm for all tested fuels. The results shown in Figure 6 indicate that thermal efficiency increased by nearly 25% and 7% for TF-1 and TF-2 test fuels at 2800 rpm compared to pure gasoline, respectively. It is clearly seen that there is a correlation between thermal efficiency and SFC.

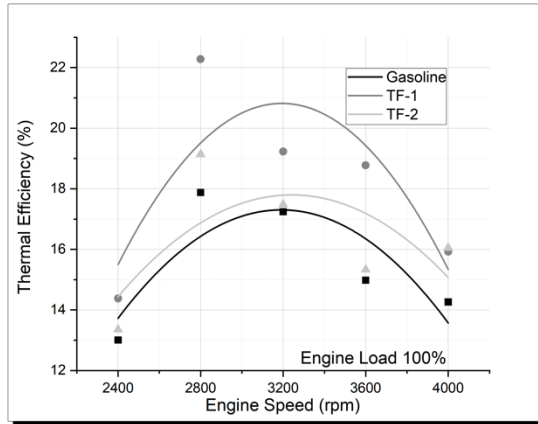


Fig. 6. The changes of thermal efficiency

The change of CO based on test fuels is given in Figure 7. CO emission levels decrease as additives are added to the fuel blends. TF-1 had the lowest CO value at 3200 rpm. CO emission values were decreased by about 5.20% and 8% with TF-1 and TF-2 fuel mixtures compared to neat gasoline at 4000 rpm. As the engine speed increases, gas temperature increases, and CO formation decreases after combustion process. CO formation tends to raise at high engine speeds due to insufficient oxygen supply to the cylinder. This can be seen in Figure 7. As the fuel additive is added, the oxidation reactions improve. Similar results for CO emission variation were presented by Kocakulak et al. [7]. Their study revealed that CO emissions were decreased as the amount of additive in the gasoline was increased. Keskin et al. also obtained similar trends in CO variations for all fuel mixtures that used benzoylthiourea derivative as a fuel additive [25].

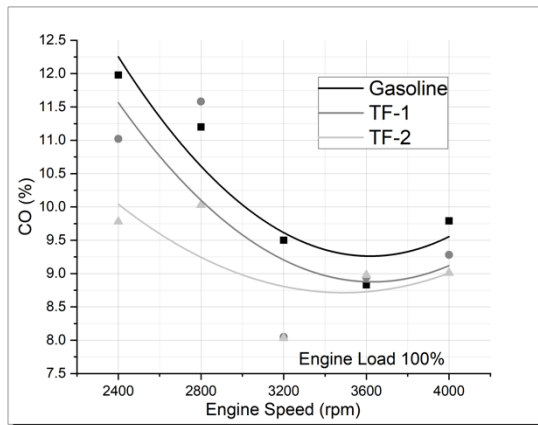


Fig. 7. CO emission variations

The influence of additive on CO₂ emissions for various engine speeds are presented in Figure 8. As the amount of additive used in the fuel mixture increases, CO₂ emissions also increase. CO formation increases and CO₂ emissions decrease due to increased pumping losses and reduced oxygen concentration in the combustion chamber at higher engine speeds, CO formation increases and

CO₂ emissions decrease. There is an inverse correlation between CO and CO₂, as illustrated in Fig. 7 and Fig. 8. The highest CO₂ was measured at 3600 rpm for all test fuels. The lowest CO₂ emission value was acquired at 2400 rpm for TF-1. CO₂ emission decreased by about 11% for TF-1 and increased by 7.2% for TF-2 fuel mixtures compared to pure gasoline.

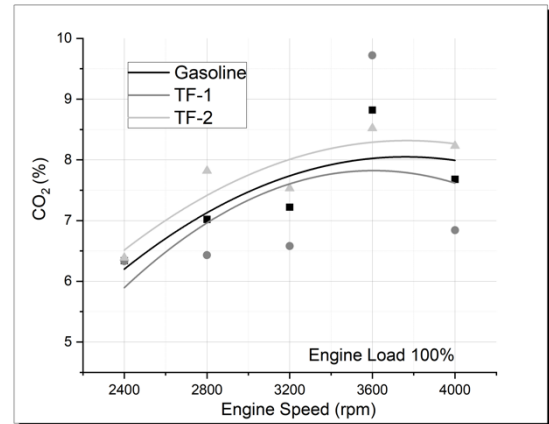
Fig. 8. CO₂ emission variations

Figure 9 represents the effects of benzoylthiourea fuel additive on HC emissions. It was observed that HC emissions raised as the fuel additive addition raised in the mixture. HC emissions decreased for both TF-1 and TF-2 compared to gasoline. The minimum HC emissions were measured for TF-1 at 3200 rpm. It was found that the emission values reduced by 22.6% and 6.2% for TF-1 and TF-2 mixtures compared to gasoline at 3200 rpm, respectively. Similarly, Keskin et al. obtained 68.15%, 34.93%, and 50.24% decrease in CO, NO_x and smoke emissions with benzoylthiourea derivative ligand as a metal additive [24].

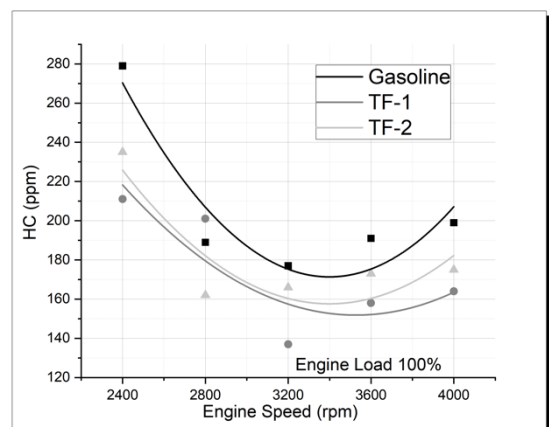


Fig. 9. HC emission variations

4. Conclusions

In this study, a previously untested benzoylthiourea derivative N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide was

used as a gasoline additive. The effects of various fuel blends on the engine performance and emissions were experimentally examined. Changes in engine torque, effective power, SFC, thermal efficiency, CO, CO₂ and HC emissions were investigated at full load and 4000, 3600, 3200, 2800, and 2400 rpm. Results are presented as follows:

- It can be generally mentioned that the addition of Benzoylthiourea Derivative Fuel N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide showed a notable performance as an additive in a spark ignition engine.
- A remarkable effect has been revealed on SFC and thermal efficiency. SFC was improved with the addition of Benzoylthiourea Derivative Fuel. Thermal efficiency increased by nearly 25% and 7% for TF-1 and TF-2 test fuels at 2800 rpm compared to pure gasoline, respectively.
- SFC decreased by approximately 19.8% and 6.6% for TF-1 and TF-2 according to gasoline at 2800 rpm respectively.
- CO reduced by about 5.20% and % with TF-1 and TF-2 fuel blends compared to gasoline at 4000 rpm.
- HC reduced by 22.6% and 6.2% for TF-1 and TF-2 mixtures compared to gasoline at 3200 rpm, respectively.
- Benzoylthiourea derivative fuel N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide can be efficiently used as an additive without modification.

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Nomenclature

<i>AC</i>	Alternative Current
<i>BSFC</i>	Brake specific fuel consumption
<i>CO</i>	Carbon monoxide
<i>CO₂</i>	Carbon dioxide
<i>C₁₃H₉BrClN₃OS</i>	N-((5-bromopyridin-2-yl)carbamothioyl)-2-chlorobenzamide
<i>DC</i>	Direct current
<i>HC</i>	Hydrocarbon
<i>PM</i>	Particulate matter
<i>SFC</i>	Specific fuel consumption
<i>NO_x</i>	Nitrogen oxides
<i>UHC</i>	Unburned hydrocarbon
λ	Lambda

Conflict of Interest Statement

The author declares that there is no conflict of interest in the study.

CRedit Author Statement

Sertaç Coşman: Conceptualization, Supervision, Conceptualization, Writing-original draft, Validation, Data curation, Formal analysis

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