

# Combined effects of hydrogen and TiO<sub>2</sub> nanoparticle additive on terebinth oil biodiesel operated diesel engine

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**Abstract.** Efforts to reduce the dependency on fossil-based fuels have intensely been researched by scientists recently. Therefore, in internal combustion engines, the usability of various alternative fuels is still being evaluated. The present study experimentally focused on the illumination of the combined impacts of nanoparticle additives and hydrogen fuel on the performance and emission characteristics of a compression ignition engine. For this purpose, diesel fuel and combinations of diesel fuel, terebinth oil biodiesel, titanium dioxides nanoparticle, and hydrogen were utilized. Reduced engine performance caused by biodiesel was compensated with the use of nanoparticles. Further improvement was also observed with hydrogen addition. Emission results showed that carbon monoxide (CO) emission values can be reduced with biodiesel, nanoparticle additive, and hydrogen since they all have positive effects to enhance combustion quality and avoid incomplete combustion. On the other hand, oxides of nitrogen (NO<sub>x</sub>) emission was increased due to a rise in cylinder temperature with the use of biodiesel, nanoparticle, and hydrogen.

**Keywords:** Biodiesel, Diesel engine, Hydrogen, Nanoparticle, Combustion.

## 1 Introduction

Both rapid increases in the world's population, industrialization, and limited reserves of conventional fuels bring huge energy requirements which cannot be met by fossil fuels alone. The unfavorable effects on the environment are another concern in order to leave the dependence on this kind of energy source. Toxic emissions released by the combustion process such as carbon monoxide, carbon dioxide, oxides of nitrogen, unburned hydrocarbons, sulphur dioxide, etc. are notorious for being very dangerous to human health and nature [1].

One of the most popular alternative energy sources to replace fossil fuels is biodiesel which can be produced by vegetable oils or animal fats with the presence of suitable catalysts and alcohol by chemical reaction [2]. Biodiesel is prominent alternative fuel since it is environmentally friendly, renewable, and biodegradable [3, 4]. On the other hand, low volatility and energy content, fuel pumping difficulties due to high viscosity and density, higher copper strip corrosion, and poor cold working conditions effectiveness are major deficiencies of biodiesel [5, 6]. Higher density of biodiesel will cause inadequate diffusion of fuel particles into

the air which may possibly bring out incomplete combustion due to insufficient mixing of fuel and air. This prevents the biodiesel from reaching the self-ignition temperature by extending the duration of the air-fuel mixing process. In addition to all this, the ignition delay period inevitably increases and the power output of the engine will be reduced, dependently [7].

Nanoparticle additives with their excellent properties have recently come into prominence to use in diesel engines in addition to base fuel. Acting as a combustion catalyst is their most featured behavior of them. High surface/volume ratio which helps further oxidation of fuel, higher enthalpy of combustion, and reduced ignition delay are the main advantages of nanoparticle usage. Totally, the use of nanoparticle additives mixed with a base fuel has the capability to meet requirements for improved performance and emission characteristics of the engine with no modifications on it [8]. Recently, the availability of various nanoparticle used in engines as additive have been searched by scientists [9–13].

Besides biofuels, another attractive energy source to be used in engines is hydrogen. There is a common belief that hydrogen will be the fuel of the future and it may possibly replace conventional fuels. Hydrogen is the most plentiful element on earth. Especially, this fuel is striking with

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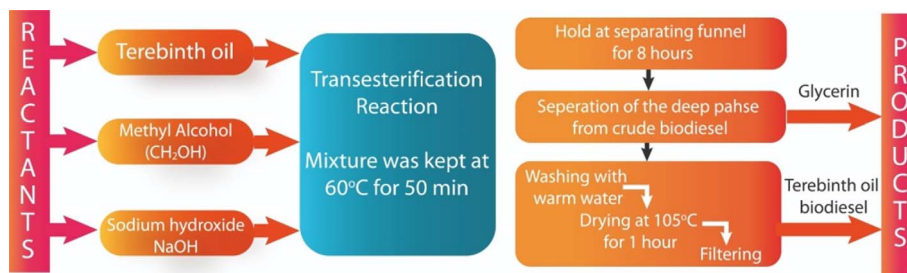


Fig. 1. Biodiesel production steps.

having a high heating value in comparison with hydrocarbon fuels [14]. The hydrogen/carbon ratio will increase by adding even a small amount of hydrogen through the engine and more flammable blends will be obtained since the high diffusivity characteristic of it. Moreover, the high flame speed of hydrogen will lessen combustion duration [15]. Environmental concerns due to the combustion of fossil fuels can readily be eliminated by the use of hydrogen as an energy source. Carbon-based pollutants (CO, CO<sub>2</sub>, soot, etc.) can be avoided depending on no carbon content and clean burning behaviors of hydrogen [16]. Lots of studies have been carried out by researchers which investigate the effects of hydrogen usage as a primary fuel in compression ignition engines [17–21].

It has been seen from the comprehensive literature survey that although the influences of both uses of various nanoparticles mixed with fuels and supplementation of pure hydrogen through the engine on performance, combustion, and emission characteristics of diesel engines have been studied many times, there is a big lack of searching which deals with the dual effects of nanoparticle and hydrogen at the same time. Therefore, the present study focused to clarify the combined impacts of nanoparticle additive and hydrogen fuel on the performance and emission characteristics of a compression ignition engine.

## 2 Materials and methods

Experiments were carried out in the *Petroleum Research and Automotive Engineering Laboratories* of the Department of Automotive Engineering at *Çukurova University*. Raw terebinth oil was utilized for the production of biodiesel via the transesterification method. First of all, the seeds of terebinth were broken into small pieces with the help of a grinding machine. Extraction of the terebinth oil from seeds was achieved with the soxhlet apparatus. At this stage, hexane was selected as a chemical solvent in order to extract oil. Lastly, drying and filtering operations for oil for purification were applied before passing through the transesterification process.

The flowchart of the biodiesel production process was demonstrated as shown in the following [Figure 1](#).

Titanium dioxide (TiO<sub>2</sub>) was commercially purchased from a firm as a nanoparticle and homogeneous distribution

of it in fuel mixtures was ensured by utilizing Sonic Vibra-Cell VC 750 model ultrasonic agitator. Mixing processes were achieved with 40% amplitude of the device.

Test fuels and additives used in this experimental study were tabulated in the following [Table 1](#) with their abbreviations.

Physicochemical properties were measured after test fuel preparation. Devices are Kyoto electronics DA-130, Zeltex ZX440, IKA Werke C2000 Bomb Calorimeter, TANAKA AKV-202 Auto Kinematic Viscosity, and Tanaka Automated Pen-sky-Martens Closed Cup Flash Point Tester APM-7 for the determination of density, cetane number, calorific value, kinematic viscosity, and flash point, correspondingly.

Performance and emission tests were conducted on a 4-cylinder with in-line configurations, a 4-stroke direct injection diesel engine. Additionally, the TiB25 mixture was exposed to hydrogen enrichment through the intake manifold of the engine with a 5 L/min flow rate to observe the hydrogen effect on performance and emission.

Torque data of the engine was gathered by a hydraulic dynamometer (*Netfren Brand*) and emissions were analyzed via an emission device called MRU Delta 1600 V. Technical specifications of test instruments were summarized in [Tables 2](#) and [3](#).

Tests were initiated after the engine was operated with diesel fuel for 15 min to reach stable engine temperature conditions. The fuel line was cleaned by operating the engine with each new fuel for a few minutes before obtaining results in order to guarantee getting rid of the remaining fuel in line with the previous experiment. Tests were executed at full load condition by varying engine speeds between 1200 and 2800 rpm with 400 rpm intervals.

## 3 Results and discussions

### 3.1 Physicochemical properties of test fuels

Determination of test fuel properties is mandatory in order to evaluate both whether they meet standards or not and the interpretation of engine test results. Test fuel properties were depicted in [Table 4](#). As seen in [Table 4](#), the fuel properties of B25 slightly changed with nanoparticle addition. D and B25 fuel properties are in accordance with the literature [22].

**Table 1.** Test fuels.

Test fuel	Diesel	Terebinth oil biodiesel	Titanium dioxides nanoparticle (TiO <sub>2</sub> )	Hydrogen (H <sub>2</sub> )
	% (on volume basis)		ppm	L/min
D	100	0	0	0
B25	75	25	0	0
TiB25	75	25	50	0
HTiB25	75	25	50	5

**Table 2.** Technical specifications of engine.

Brand	<i>Mitsubishi canter</i>
Model	4D34-2A
Configuration	In line 4
Type	Direct Injection
Displacement	3907 cc
Bore/Stroke	104/115 mm
Maximum power	89 kW @ 3200 rpm
Maximum torque	295 Nm @ 1800 rpm

### 3.2 Performance characteristics of engine

In the following Figures 2–4, torque, power, and Specific Fuel Consumption (SFC) variations with respect to engine speed as a performance indicator of the engine can be seen.

The average reduction in engine torque and power values were observed for B25 as 5.04% and 5.22% compared to diesel fuel. It is a very well-known phenomenon that pure or mixed biodiesel utilization in the engine as fuel cause to reduced levels of torque and power since it has low calorific value and poorer atomization due to its higher viscous nature of it [23–25]. In comparison with diesel fuel, increment values for torque and power were 2.43% and 2.17% for TiB25. Besides that, torque and power increments levels were 10.18% and 8.26% for HTiB25. These all improvements can be explained by high energy content, the high surface-volume ratio for enhanced oxidation and catalyst effect of nanoparticles [26], and the high energy content of hydrogen fuel with faster flame speed [17].

As known, SFC is a very effective indicator in order comparing the engines operated by various fuels using fuel economy. It exhibits the fuel consumed for the unit power generation. The reasons explained above for reduced power bring expectations for increased SFC with the use of biodiesel. It means that much more fuel has to be consumed for the production of unit power owing to lower values of calorific value and higher density of biodiesel [27]. The average increment in SFC was observed as 6.82% for B25 compared to diesel fuel. The lower SFCs were obtained with ratios of 3.37% and 9.68% for the TiB25 and HTiB25, respectively, according to diesel fuel. The increased SFC with the use of B25 can be compensated by the noteworthy properties of TiO<sub>2</sub> nanoparticles such as behaving as oxygen buffer for supplementation of extra oxygen content during combustion [12] and features of hydrogen such as

**Table 3.** Exhaust emission measurement rates and accuracy levels of device.

Emission	Range of measurement	Accuracy
CO	0–4000 ppm	±20 ppm
CO <sub>2</sub>	0–20%	±0.5%
NO	0–4000 ppm	±5 ppm
NO <sub>2</sub>	0–1000 ppm	±5 ppm

higher calorific value and superior combustion characteristics [28] which triggers reduced fuel consumption with increased power.

### 3.3 Emission characteristics of engine

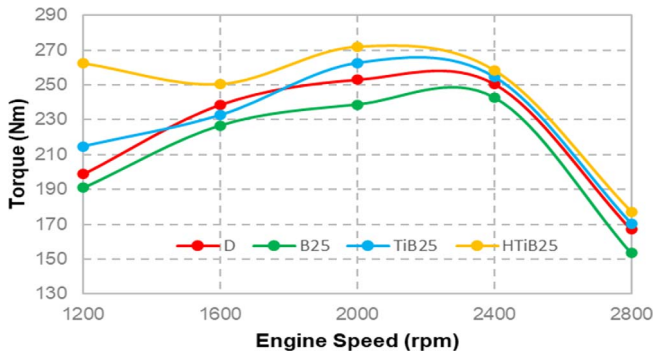
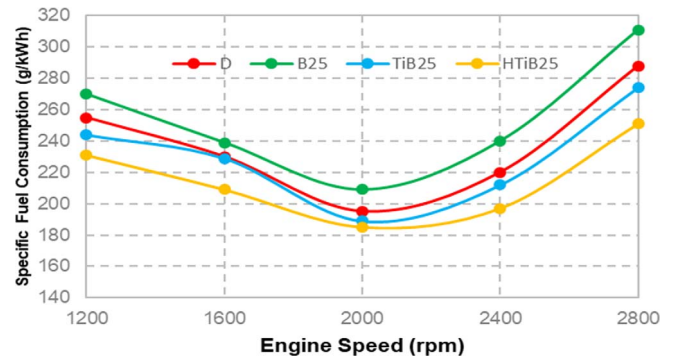
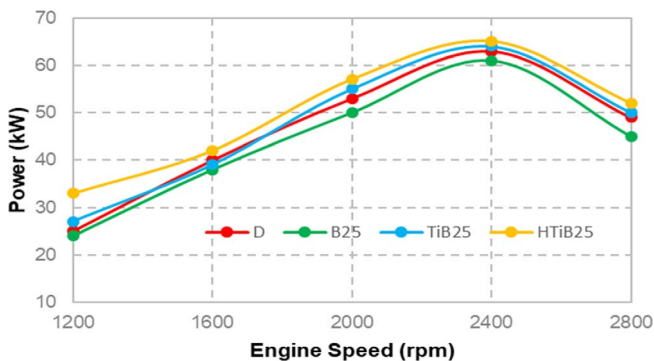
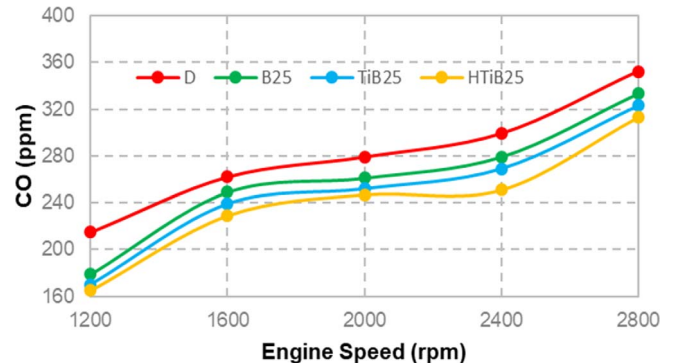
Changes in carbon monoxide (CO) and oxides of nitrogen (NO<sub>x</sub>) concerning engine speed were presented in the following Figures 5 and 6.

Incomplete combustion which means that there is not enough oxidizer for the conversion of CO to CO<sub>2</sub> causes to increase in CO emission which is very toxic to human health. Engine operation with a fuel-rich mixture is mainly responsible for the generation of these pollutants [29]. Biodiesel contains excessive oxygen content in its molecular structure and this situation makes biodiesel very famous environmentally for its extra oxidation capability which helps to reduce CO emissions [30, 31]. CO emissions were observed to reduce nearly by 7.53% with B25 usage during engine tests compared to diesel fuel. There is a good harmony between the obtained results and the literature [22, 23, 32]. In comparison to diesel fuel, average reductions in CO were observed as 10.95% and 14.36% for TiB25 and HTiB25, correspondingly. Improvements in CO can be explained by the presence of nanoparticles by enhanced combustion as a result of oxygen buffering action [33]. Further amelioration of CO was achieved with the use of hydrogen due to the lack of carbon atoms in its structure [34].

One of the major drawbacks of biodiesel is releasing much more NO<sub>x</sub> emissions than conventional diesel fuel. NO<sub>x</sub> emissions have adverse effects on both environment and human health. Cylinder pressure, temperature, duration of combustion, air-fuel ratio, the oxygen content of the fuel and humidity, etc. are the factors that affect the constitution of NO<sub>x</sub> [35]. An increment in NO<sub>x</sub> emissions of 9.37% was seen for B25 compared to pure diesel fuel. The possible cause of this rise is better combustion obtained

**Table 4.** Physicochemical properties of test fuels.

Test fuels and standards	Property				
	Density (kg/m <sup>3</sup> )	Cetane number	Calorific value (MJ/kg)	Viscosity at 40 °C (cSt)	Flash point (°C)
D	835	53.7	45.6	2.75	65
EN590	820–845	Min. 51	–	2.0–4.5	Min. 55
B25	838	55.2	44.1	3.7	82
TiB25	842	58	44.3	3.75	83
EN14214	860–900	Min. 51	–	3.5–5.0	Min. 120
Hydrogen [17]	0.0837	–	119.93	–	–

**Fig. 2.** Torque *versus* engine speed.**Fig. 4.** Specific fuel consumption *versus* engine speed.**Fig. 3.** Power *versus* engine speed.**Fig. 5.** CO *versus* engine speed.

in the cylinder which enables to increase in combustion temperature as a result of the oxygen content of biodiesel [36]. In comparison to diesel fuel, average increments in NO<sub>x</sub> were observed as 11.21% and 15.69% for TiB25 and HTiB25, respectively. Increments of NO<sub>x</sub> can be explained by the presence of nanoparticles by the catalytic effect of particles which enable large surface/volume areas for enhanced combustion and increased temperature [37]. Further rise in NO<sub>x</sub> was caused by the use of hydrogen due to increased adiabatic flame temperature compared to petrol-based fuels which contribute to increased combustion temperature. Combustion duration is shortened owing to the higher flame speed of hydrogen [38].

Results showed that both the performance and emission characteristics of diesel engines were improved by the presence of nanoparticles and further improved with the aspiration of hydrogen through the intake manifold, additionally. Deterioration only occurs on NO<sub>x</sub> emissions. It can also be lowered by using one of the most effective methods for NO<sub>x</sub> reduction such as Exhaust Gas Recirculation (EGR), Lean NO<sub>x</sub> Trap (LNT), and Selective Catalytic Reduction (SCR) [39]. The addition of water into prepared fuels in order to obtain water-emulsified fuels can be another suggested method for the possible reduction of NO<sub>x</sub> emissions with no engine modification [40].

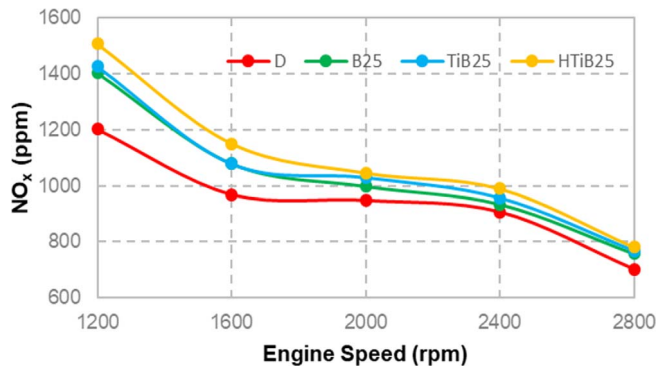


Fig. 6. NO<sub>x</sub> versus engine speed.

## 4 Conclusion

Compared to diesel fuel, B25 showed 5.04% and 5.22% reduction values on torque and power while a 6.82% increment on SFC. Increment ratios on torque were 2.43% and 10.18%, on power were 2.17% and 8.26% and the ratios of reduction on SFC were 3.37% and 9.68% with the use of TiB25 and HTiB25 in comparison to diesel, respectively.

Reduction in torque and power, increment on SFC caused by biodiesel can be compensated with the nanoparticle addition. It has been thought that the high energy content and surface-volume ratio for enhanced oxidation and catalyst effect of nanoparticles were the key factors for performance improvements. Hydrogen can further enhance these performance characteristics via high energy content with the faster flame speed of hydrogen.

Average reductions of 7.53%, 10.95%, and 14.36% were achieved for B25, TiB25, and HTiB25, respectively compared to diesel fuel, in terms of CO emissions.

Extra oxygen content in the molecular structure of biodiesel has led to obtaining lowered CO compared to diesel. Further improvement in CO may be achieved with the oxygen-buffering action of nanoparticles and the lack of carbon atoms in the structure of hydrogen.

In terms of emissions NO<sub>x</sub> emissions, average increments of 9.37%, 11.21%, and 15.69% were observed for B25, TiB25, and HTiB25, respectively compared to diesel fuel.

These all increments can be explained by improved combustion due to the oxygen content of biodiesel, the catalytic effect of nanoparticles, and the higher flame speed of hydrogen.

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