Journal of Tekirdag Agricultural Faculty
Tekirdağ Ziraat Fakültesi Dergisi

Aralık/December 2022, 19(4)
Başvuru/Received: 18/02/22
Kabul/Accepted: 19/10/22
DOI: 10.33462/jotaf.1075550

http://dergipark.gov.tr/jotaf
http://jotaf.nku.edu.tr/

ARAŞTIRMA MAKALESİ **RESEARCH ARTICLE**

Determination of the Effects of Some Additives Added to the Mixture of Diesel and Safflower Biodiesel on Exhaust Emissions*

Motorin ve Aspir Biyodizeli Karışımlarına İlave Edilen Bazı Katkı Maddelerinin Egzoz Emisyonlarına Etkilerinin Belirlenmesi

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Abstract

In this study, linas, a newly developed variety of safflower plant, were used for biodiesel production. Fuel properties and exhaust emission values of biodiesel fuel (B_{100}) and alternative blended fuels containing different volumetric amounts of diesel (M_{100}), biodiesel (B_{100}) and n-butanol (BU) or n-pentanol (P) (diesel / biodiesel / n-butanol and diesel / biodiesel / n-pentanol) were evaluated in comparison with the reference fuel diesel (M_{100}). In addition, in the study, the effects of 2-ethylhexyl nitrate (EHN) on fuel properties and emission values have been examined by adding EHN cetane improver additive to mixture fuels at a concentration of 2000 ppm. Exhaust emission tests of all fuels and mixtures were carried out in a four-cylinder, four-stroke, and direct injection diesel engine at different speeds and full load conditions. According to the results of the research, the fuel properties of diesel, biodiesel, and blended fuels have been determined that comply with biodiesel and diesel fuel standards. Density values of these fuels were determined between 0.830 to 0.8885 kg m^{-3}, kinematic viscosities 2.83 and 4.57 mm^2s^{-1}, calorific values 40.13 and 43.4 MJ kg^{-1}, water content 48.015 and 499 ppm, cetane numbers 48.8 and 55.8, cloud point, cold filter plugging point, and pour point -13.9 and -1.4 ºC, -22 and -10 ºC, -15 and <-20 ºC, respectively. While CO, CO_2, and NO_x emissions of blended fuels show lower values compared to diesel fuel, it has been determined that there are certain rates of increases in HC and O_2 emissions. It was determined that the high NOx emissions of biodiesel decreased with the addition of high alcohols to the blend fuels. In general, it has been determined that the fuel properties and emission results of blends containing pentanol show better results than fuels containing butanol. The 2-Ethylhexyl Nitrate additive used in the blend was effective in improving the emissions.

Keywords: 2-ethylhexylnitrate, Biodiesel, Exhaust emission, n-butanol, n-pentanol.

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Atıf/Citation: Şahin S., Mengeş, H.O. Determination of the effects of some additives added to the mixture of diesel and safflower biodiesel on exhaust emissions *Tekirdağ Ziraat Fakültesi Dergisi,* 19(4), 769-787.

*This article is summarized from Seda Şahin's Ph.D. Thesis.

Öz

Bu çalışmada, biyodizel üretimi için aspir bitkisinin yeni geliştirilmiş bir çeşidi olan linas kullanılmıştır. Biyodizel (B_{100}) yakıtı ve hacimsel olarak farklı oranlarda motorin (M_{100}), biyodizel (B) ve n-bütanol (BÜ) veya n-pentanol (P) ihtiva eden alternatif karışım yakıtlarının (motorin/biyodizel/ n-bütanol ve motorin/biyodizel/ n-pentanol), yakıt özelikleri ve egzoz emisyon değerleri referans yakıt motorin (M_{100}) ile karşılaştırmalı olarak değerlendirilmiştir. Araştırmada ayrıca karışım yakıtlarına 2000 ppm konsantrasyonunda 2-etilhekzil nitrat (EHN) setan iyileştirici katkısı ilave edilerek EHN'nin yakıt özellikleri ve emisyon değerlerine etkileri incelemiştir. Tüm yakıt ve karışımlarına ait egzoz emisyon testleri, dört silindirli, dört zamanlı ve direkt enjeksiyonlu bir dizel motorda farklı hızlarda ve tam yük koşullarında gerçekleştirilmiştir. Araştırma sonuçlarına göre motorin, biyodizel ve karışım yakıtlarına ait yakıt özelliklerinin, biyodizel ve motorin yakıtı standartlarıyla uyum içerisinde olduğu tespit edilmiştir. Bu yakıtlara ait yoğunluk değerleri 0.830 ile 0.8885 kg m^{-3}, kinematik viskoziteleri 2.83 ile 4.57 mm^2s^{-1}, ısıl değerleri 40.13 ile 43.4 MJ kg^{-1}, su içerikleri 48.015 ile 499 ppm, setan sayıları 48.8 ile 55.8, bulutlanma, SFTN ve akma noktaları ise sırasıyla-13.9 ile -1.4 ºC, -22 ile -10 ºC, -15 ile <-20 ºC arasında belirlenmiştir. Karışım yakıtlarına ait CO, CO_2 ve NO_x emisyonları motorin yakıtına göre daha düşük değerler gösterirken, HC ve O_2 emisyonlarında ise belli oranlarda artışlar olduğu tespit edilmiştir. Karışım yakıtlarına yüksek alkollerin eklenmesiyle biyodizelin yüksek olan nox emisyonlarının düştüğü belirlenmiştir. Genel olarak pentanol ihtiva eden karışımların yakıt özellikleri ve emisyon sonuçlarının bütanol ihtiva eden yakıtlara göre daha iyi sonuçlar gösteriği tespit edilmiştir. Karışımlarda kullanılan 2-Etilhekzil Nitrat katkı maddesi emisyonları iyileştirmede etkili olmuştur.

Anahtar kelimeler: 2-etilhekzilnitrat, Biyodizel, Egzoz emisyonu, n-bütanol, n-pentanol

1. Introduction

Energy is one of the most important consumption items of our age and an indispensable civilization tool. Energy consumption, which is one of the most important needs of countries with a high level of development, tends to increase continuously. Therefore, countries need to produce and use renewable energy sources in order to meet their energy needs without harming the environment. The concepts of biomass, biofuel and bioenergy are very broad and interact with each other. Bioenergy can be produced from biomass as solid, liquid and gas.

Agricultural products constitute the source of biofuel energy, which has an important potential among renewable energy sources. These products consist of oilseed crops such as sunflower, rapeseed, soybean, safflower, cotton; carbohydrate crops such as potatoes, wheat, barley, rye, maize, sugar beet, sugarcane, sweet sorghum; fiber plants such as flax, kenaf, hemp, miscanthus (elephant grass). In addition to these plants, agricultural residues such as branches, stems, straw, roots, bark and animal residues are also used in biofuel production (Narin, 2008).

In recent years, the use of fossil fuels in the industry and transportation sector has led to an increase in Greenhouse Gas emissions and global warming (Jiaqiang et al., 2019; Öğüt et al., 2022). Since changes in engine design to reduce harmful emissions will be costly, the use of alternative fuels, which are less polluting than petroleum and its derivatives, has gained great importance in internal combustion engines (Kaplan et al., 2009; Özer, 2014). Liquid fuels are used in the transportation sector, which has a large share in world energy consumption. Vegetable oils, biodiesel produced from these vegetable oils, and bioalcohols produced from biomass are the leading liquid biofuels that can be used as an alternative to fossil-based liquid fuels (Yılmaz and Atmanlı, 2016).

They can also be used as fuel additives to increase the low-temperature fluidity of biodiesel (Atmanlı et al., 2015; Li et al., 2015; Şahin et al., 2015). Higher alcohols such as butanol (C4) and pentanol (C5) can be considered as competitive alternative fuels today due to their liquid nature, high oxygen content and production from renewable biomass. (Kumar and Saravanan, 2016). Higher alcohols are effective to reduce properties such as kinematic viscosity and density. In order to meet the increasing energy demand and control environmental pollution, sustainable policies have begun to be adopted that allow diesel fuels to be mixed with biodiesel, biobutanol, biopentanol or such fuels with diesel fuel (Kumar and Saravanan, 2016).

There are 15 safflower cultivars (Yenice 5-38, Dinçer 5-18-1, Remzibey-05, Zirkon, Balcı, Linas, Olas, Göktürk, Asol, Hasankendi, Yektay, Zirkon, Olein, Koç, Safir and Servetağa) registered as domestic seeds in Turkey (Arslan et al., 2019; Culpan and Arslan, 2022). Linas variety safflower plant has a spiny structure, flower color is yellow-orange and seed color is cream color. The average yield is 300-350 kg da^{-1}, the average oil content (within the seed) is 37-38%, and linoleic and oleic fatty acids are 71% and 18%, respectively. Linas variety safflower plant was registered by Trakya Research Institute in 2013 (Arslan et al., 2019). As the linas variety safflower plant used in this study is resistant to cold, it is suitable for the climatic conditions of Turkey. The most distinctive feature of safflower oil is that it has low saturated fatty acids and high unsaturated fatty acids (Arslan and Bayraktar, 2016). In addition, high oil and fatty acid ratios are suitable for biodiesel production. The physico-mechanical properties of Linas variety safflower seed are given in *Table 1*.

Keskin et al. (2013) examined the engine performance and exhaust emission values of fuel A (60% diesel, 30% biodiesel, 5% ethanol, 5% butanol) and fuel B (40% diesel–50% biodiesel–5% ethanol–5% butanol) mixture fuels, which they tested in a single-cylinder, four-stroke diesel engine under full load conditions, in comparison with diesel fuel. As a result of the study, they stated that the emission values of the blended fuels showed a significant improvement compared to the diesel fuel and that the emission values of fuel B, carbon monoxide (CO) and, hydrocarbon (HC), decreased by 87.01% and 87.50%, respectively.

Atmanlı (2016a) used diesel fuel (D), waste oil biodiesel (B) and propanol (Pro), n-butanol (nB), and 1-pentanol (Pn) fuels, which are in the high alcohol group, as fuel mixtures. Determined the effects on engine performance and exhaust emission values in a 4-cylinder turbocharged and water-cooled diesel engine. He stated that the addition of alcohol to the mixtures decreased the NO_X emission values, however, it increased the CO emissions. In addition, when the researcher compared the blend fuels in terms of HC emission reduction, it was determined that the D40B40Pn20 fuel gave the best results.

Table 1. Some physico-mechanical properties of safflower (linas variety) seed

Class	Name	Unit	Values
Geometric Properties	Thickness	(mm)	2.99± 0.23
	Width	(mm)	4.01± 0.44
	Lenght	(mm)	7.47± 0.63
	Geometric mean diameter	(mm)	4.46± 0.26
	Sphericity	(%)	59.94± 3.36
	Projected area	(mm^2)	26.17
Gravimetric Properties	Porosity	(%)	40.68
	Density	(g lt^{-1})	549±9.65
	Mass of 1000 seeds	(g)	39.72± 0.75
Aerodynamic Characteristic	Terminal velocity	(m s^{-1})	3.77± 0.27
Mechanical Property	Fracture resistance	(N mm^{-2})	10.65± 1.43
Chemical Properties	Moisture (% w.b.)	(%)	5.6

İleri (2016) aimed to investigate the effect of EHN addition on fuel properties, engine performance, and exhaust emission values of blended fuels by adding cetane improver 2-Ethylhexyl nitrate (EHN) at 500, 1000, and 2000 ppm concentrations to D70S20B10 (70% diesel, 20% sunflower oil and 10% n-butanol) and D70S20P10 (70% diesel, 20% sunflower oil and 10% 1-pentanol) blended fuels. It was determined that the NOx values of the blended fuels with the addition of EHN decreased by 0.26% to 5.26%. He stated that CO emissions increased by 7.16% to 23.46% depending on the increase in EHN concentration. Compared to diesel fuel, D70S20B10 and D70S20P10 blended fuels reported increases of 133.29% and 153.1%, respectively, in HC emissions.

Örs (2016) investigated the effects of diesel fuel, soybean oil biodiesel, and butanol blends on engine performance and exhaust emissions in a single-cylinder direct injection diesel engine. Mixture fuels were obtained by adding 5% (BU5), 10% (BU10), and 15% (BU15) butanol to soybean oil biodiesel (BU0) by volume. It was stated that the addition of 15% butanol (BU15) to soybean oil biodiesel reduced NOx, particulate matter (PM), and CO emissions by 16%, 24%, and 49%, respectively, compared to diesel fuel. It was determined that the HC emission and specific fuel consumption values (average 10%) increased as the butanol ratio increased in the blended fuels.

In this study, biodiesel (B_{100}) fuel and alternative blended fuels (diesel/biodiesel/n-butanol and n-butanol) containing diesel (M_{100}), biodiesel (B) and n-butanol (BU) or n-pentanol (P) in different volumetric ratios were investigated. It is aimed to evaluate the fuel properties and exhaust emission values of these fuels in comparison with the reference fuel diesel (M_{100}). The study also investigated the effects of EHN on fuel properties and emission values by adding 2-ethylhexyl nitrate (EHN) cetane improver additive at a concentration of 2000 ppm to the blend fuels. Linas variety safflower is a newly developed variety and there is no biodiesel study on this subject. High alcohol additives were used to improve the kinematic viscosity and cold flow properties of safflower biodiesel. Since it was recommended to use less than 20% of these high alcohols in previous studies, the rates were determined accordingly. Since high alcohol addition reduces the cetane number, the effect of EHN additive as cetane improver was investigated.

2. Materials and Methods

The study consists of the following steps. These;

• Obtaining oil from safflower seeds; Extraction of oil from safflower (linas variety) seed was carried out in 3 stages as crushing, annealing and squeezing. The seeds were first pre-treated in a crushing machine and then heated and annealed, cold pressed in a 200-ton hydraulic press to obtain oil and pulp.

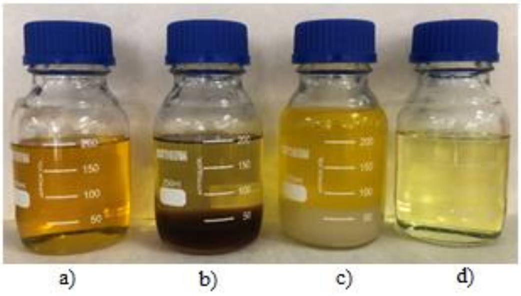
• Production of safflower oil methyl ester (biodiesel) from the obtained crude safflower (linas variety) oil by transesterification method, preparation of mixtures ($M_{85}B_{10}BU_{5}$, $M_{80}B_{10}BU_{10}$, $M_{70}B_{10}BU_{20}$, $M_{75}B_{20}BU_{5}$, $M_{70}B_{20}BU_{10}$, $M_{60}B_{20}BU_{20}$) containing diesel, biodiesel (10% and 20%) and n-butanol (5%, 10% and 20%) by volume, preparation of mixtures containing diesel, biodiesel (10% and 20%) and n-pentanol (5%, 10% and 20%) by volume $M_{85}B_{10}P_5$, $M_{80}B_{10}P_{10}$, $M_{70}B_{10}P_{20}$, $M_{75}B_{20}P_5$, $M_{70}B_{20}P_{10}$, $M_{60}B_{20}P_{20}$),

• Obtaining mixed fuels with EHN addition by adding 2000 ppm 2-ethylhexyl nitrate (EHN) to all prepared fuel mixtures ($M_{85}B_{10}BU_5$+EHN, $M_{85}B_{10}P_5$+EHN, $M_{80}B_{10}BU_{10}$+EHN, $M_{80}B_{10}P_{10}$+EHN, $M_{70}B_{10}BU_{20}$+EHN, $M_{70}B_{10}P_{20}$+EHN, $M_{75}B_{20}BU_5$+EHN, $M_{75}B_{20}P_5$+EHN, $M_{70}B_{20}BU_{10}$+EHN, $M_{70}B_{20}P_{10}$+EHN, $M_{60}B_{20}BU_{20}$+EHN, $M_{60}B_{20}P_{20}$+EHN), exhaust emission tests were carried out of reference fuel diesel, biodiesel, and blended fuels. All fuel blends were mixed homogeneously before starting the experiments.

2.1. Biodiesel Production

Biodiesel production from safflower oil was made by transesterification method. In the production of safflower (linas variety) oil methyl ester (biodiesel), PLC supported pilot production facility which was established within the scope of DPT 2004/7 project at Selçuk University Faculty of Agriculture, Department of Agricultural Machinery and Technologies Engineering was used (Öğüt et al., 2004).

Figure 1 shows the methyl ester (biodiesel) production stages of safflower oil produced by the transesterification method from crude safflower oil.



(a) crude oil (b) glycerol (c) wash water (d) biodiesel

Figure 1. Safflower (linas variety) oil methyl ester (biodiesel) production steps

To produce biodiesel, methoxide was obtained by mixing 20% of crude safflower oil with methyl alcohol (CH_3OH) and 3.5g of NaOH per liter of oil. Crude safflower oil was heated to 55ºC and methoxide was added to it. It was waited for 8 hours for the glycerol in the oil, which was mixed for 60 minutes, to precipitate and the glycerol was separated. The temperature was increased up to 75ºC and the remaining methyl alcohol in the crude biodiesel was removed. Washing process was applied at 50ºC and wash water was separated from methyl ester. Finally, drying process at 100ºC was applied and biodiesel was obtained.

2.1.1 Preparation of fuel blends

Blended fuels without EHN were prepared by homogeneously mixing diesel, biodiesel, and n-butanol ($C_4H_{10}O$) and n-pentanol ($C_5H_{12}O$), which are in the high alcohol group, at certain volumetric ratios with a homogenizer. In addition, mixed fuels with EHN addition were obtained by adding 2000 ppm cetane improver 2-Ethylhexyl nitrate (EHN) to these blend fuels, which were re-prepared at the same volumetric proportions. Diesel fuel is symbolized as "M", safflower biodiesel "B", n-butanol "BU", n-pentanol "P", and 2- Ethylhexyl nitrate "EHN" for ease of use. The numbers added in the form of indices under the symbols represent the mixing ratios of the fuels.

2.1.2 Determination of fuel properties

In the study, kinematic viscosity, density, calorific value, water content, flash point, cloud point, cold filter plugging point, pour point, copper strip corrosion tests of safflower biodiesel and blended fuels were performed. Fuel properties have been determined according to the device and working methods given in *Table 2*.

Table 2. Specifications of Test Devices

Fuel Characteristic	Devices	Measuring range	Unit	Measuring accuracy	Manufacturer	Standard
Density	Kem Kyoto DA-130N	0.0000 - 2.0000	g cm^{-3}	±0.0001	Kem Kyoto Electronic, Japan	EN ISO 3675 EN ISO 12185
Kinematic viscosity	Koehler K23377	Ambient temperature – 150	ºC	±0.01	Koehler Instrument Company, US	EN ISO 3104
Flash point	Koehler K16270	Ambient temperature - 370	ºC	±0.01	Koehler Instrument Company, USA	EN ISO 2719 EN ISO 3679
Water content	Kem Kyoto MKC-501	10µg-100mg	µg	±0.01	Kem Kyoto Electronic, Japan	EN ISO 12937
Calorimeter	IKA C 200	0-40.000	J	±0.0001	IKA, UK	DIN 51900
Cold filter plugging point	Tanaka AFP-102	With refrigerant down to -60ºC	ºC	±0.01	Tanaka Scıentıfıc Lımıted, Japan	EN ISO 3015 EN ISO 3016
Copper strip corrosion	Koehler K 25330	0-190	°C	±0.01	Koehler Instrument Company, USA	EN ISO 2160
Cetane Number	Core Lab CFR Dresser	0- 100			Core Lab CFR Dresser, USA	ASTM D 613-18

2.2 Test unit

The engine tests carried out to determine the exhaust emission values of diesel, safflower biodiesel, and blended fuels were carried out in the engine test set up within the Department of Agricultural Machinery and Technologies Engineering, Faculty of Agriculture, Selçuk University. Test setup; It consists of engine, hydraulic dynamometer, magnetic pick-up, S type load cell, fuel meter, exhaust emission device and control unit. The tests were carried out on a 4-stroke, 4-cylinder, direct injection diesel engine with a turbocharger system. After the test engine was ready for the tests, full load-differential speed tests were applied to the test engine in order to determine the exhaust emission values of the fuels. Technical specifications of the diesel engine used in the research are given in *Table 3*.

Table 3. Technical specifications of the diesel engine used in the research

Name	Technical specifications
Brand and model	Tümosan 4DT-39T-185C
Rated Power @2300 rpm	85 HP
Maximum torque	340 Nm
Total Engine Capacity	3908 cm^3
Diameter Stroke	104 mm x 115 mm
Number of Cylinders	4
Minimum Specific Fuel Consumption	160 g HPh^{-1}
Aspiration	Turbocharger
Number of Valves Per Cylinder	2
Compression Ratio	17:01
Combustion System	Direct Injection
Cooling system	Water Cooled

2.2.1 Exhaust emission measuring device

"Mobydic" brand exhaust emission device was used in the exhaust emission measurements of the test material fuels. The transmission of the exhaust emission data to the device was carried out by a probe attached to the exhaust outlet. The technical features of the emission device are shown in *Table 4*.

Table 4. Technical Specifications of Exhaust Emission Device

Measurement Parameters	Unit	Measurement range
CO	ppm	0 – 10
CO_2	%Vol	0 – 20
HC	ppm	0 - 20000
O_2	%Vol	0 – 21
NO_x	ppm	0 – 5000

3. Results and Discussion

3.1 Fuel Properties

Necessary tests were carried out to determine the compliance of the obtained safflower biodiesel with EN 14214 and diesel fuel with TS 3082 EN 590 standards. The results of the analysis are given in *Table 5* and it has been found that the fuel properties are in accordance with the standards. In the measurements made, the viscosity of safflower biodiesel is 4.57 $mm^2 s^{-1}$, its flash point is 160^o C and its density is 0.888 g cm^{-3}, which is within the limit values according to EN 14214. In the copper strip corrosion test, 1a indicates light orange, almost the same colour as the newly polished strip. The kinematic viscosity values decreased with the use of butanol and pentanol higher alcohols. EHN contribution, on the other hand, was effective in increasing the heating values and cetane numbers.

Table 5. Fuel properties of safflower biodiesel and blended fuels

Fuels	Kinematic viscosity ($mm^2 s^{-1}$)	Density (g cm^{-3})	Water content (ppm)	Calorific Values (Mj kg^{-1})	Flash Point (^{o}C)	CFPP (^{o}C)	Cloud Point (^{o}C)	Pour Point (^{o}C)	Cetane Numbers	Copper Strip Corrossion
M_{100}	2.97	0.830	48	45.17	68	-22	-13.9	>-20	55.4	1a
B_{100}	4.57	0.8885	363	40.67	160	-11	-2.6	-15	53.6	1a
$M_{85}B_{10}BU_5$	2.81	0.8379	368	43.84	38	-13	-3.2	>-20	52.3	1a
$M_{85}B_{10}BU_5$+EHN	2.8	0.8377	358	44.01	39	-11	-2.1	>-20	54.9	1a
$M_{80}B_{10}BU_{10}$	2.66	0.8368	489	43.24	37	-12	-3.2	>-20	51.9	1a
$M_{80}B_{10}BU_{10}$+EHN	2.65	0.8365	470	43.43	38	-11	-2.2	>-20	54.7	1a
$M_{70}B_{10}BU_{20}$	2.54	0.8339	499	42.40	36	-12	-3.2	>-20	49.2	1a
$M_{70}B_{10}BU_{20}$+EHN	2.52	0.8337	425	43.21	37	-11	-2	>-20	49.7	1a
$M_{75}B_{20}BU_5$	2.81	0.8384	347	43.23	39	-13	-3.2	>-20	52.1	1a
$M_{75}B_{20}BU_5$+EHN	2.76	0.8382	325	43.86	40	-11	-2.5	>-20	55.3	1a
$M_{70}B_{20}BU_{10}$	2.79	0.8375	354	42.78	38	-12	-2.5	>-20	51.3	1a
$M_{70}B_{20}BU_{10}$+EHN	2.75	0.8372	347	43.31	39	-10	-1.4	>-20	53.4	1a
$M_{60}B_{20}BU_{20}$	2.62	0.8351	410	41.42	37	-12	-3.4	>-20	48.8	1a
$M_{60}B_{20}BU_{20}$+EHN	2.57	0.8348	406	42.10	38	-11	-2.3	>-20	49.3	1a
$M_{85}B_{10}P_5$	2.83	0.8388	332	43.91	50	-14	-3.3	>-20	52.5	1a
$M_{85}B_{10}P_5$+EHN	2.82	0.8382	326	44.10	51	-12	-2.4	>-20	55.8	1a
$M_{80}B_{10}P_{10}$	2.76	0.8375	350	43.50	49	-13	-3.3	>-20	52.2	1a
$M_{80}B_{10}P_{10}$+EHN	2.74	0.8373	333	43.96	50	-11	-2.6	>-20	55.4	1a
$M_{70}B_{10}P_{20}$	2.75	0.8347	384	42.68	48	-13	-3.5	>-20	49.5	1a
$M_{70}B_{10}P_{20}$+EHN	2.66	0.8342	363	42.77	49	-10	-2.7	>-20	50.4	1a
$M_{75}B_{20}P_5$	2.82	0.8383	426	43.84	51	-14	-3.5	>-20	52.5	1a
$M_{75}B_{20}P_5$+EHN	2.78	0.8381	397	43.96	52	-12	-2.2	>-20	55.6	1a
$M_{70}B_{20}P_{10}$	2.81	0.8379	439	43.64	50	-13	-4.2	>-20	51.5	1a
$M_{70}B_{20}P_{10}$+EHN	2.8	0.8375	403	43.84	51	-12	-2.9	>-20	53.9	1a
$M_{60}B_{20}P_{20}$	2.71	0.8367	493	42.49	49	-13	-4.2	>-20	49.3	1a
$M_{60}B_{20}P_{20}$+EHN	2.7	0.8362	461	42.88	50	-11	-3	>-20	50.7	1a

3.2 Exhaust Emission Test Results

3.2.1 Change of carbon monoxide (CO) values

The variation of CO emission values of diesel (M_{100}), biodiesel (B_{100}), and blended fuels (EHN added – non-additive) in exhaust emission tests performed under full load conditions depending on engine revolution speed (min^{-1}) given in *Figures 2, 3* and *4.*

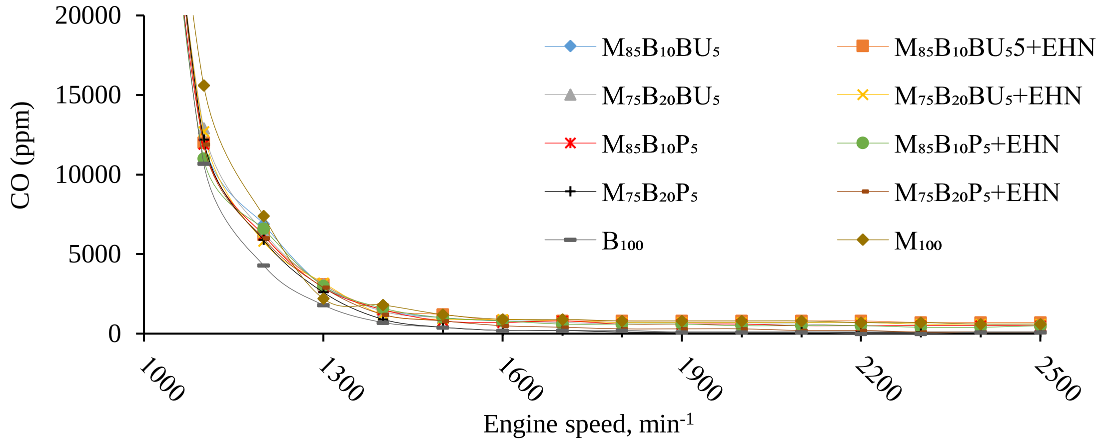


Figure 2. Change in carbon monoxide (CO) emission values of M_{100}, B_{100}, and mixed fuels (containing 5% BU or P) depending on engine speed

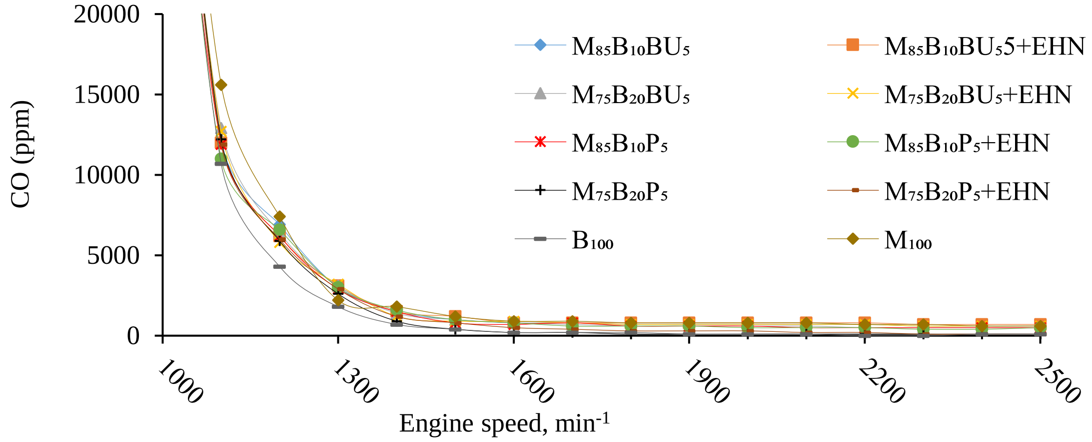


Figure 3. Change in carbon monoxide (CO) emission values of M_{100}, B_{100}, and mixed fuels (containing 10% BU or P) depending on engine speed

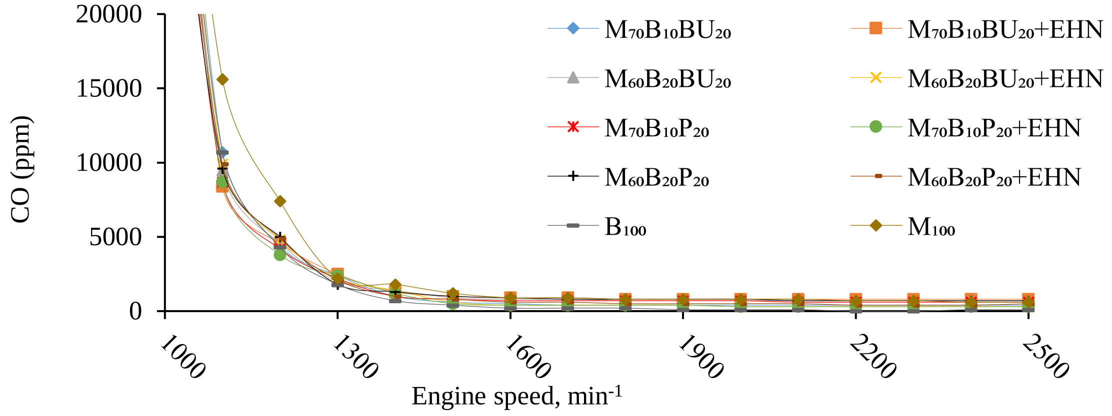


Figure 4. Change in carbon monoxide (CO) emission values of M_{100}, B_{100}, and mixed fuels (containing 20% BU or P) depending on engine speed

As a result of the comparison of the values of diesel (M_{100}) and safflower biodiesel (B_{100}) fuels, the CO emission values of M_{100} fuel showed higher values than B_{100} were determined that at all engine speeds. In addition, the difference between the values of both fuels decreased depending on the increase in the engine speed. While the CO emission value of B_{100} fuel was 1800 ppm at 1300 min^{-1} engine speed at which the maximum engine torque has obtained, this value increased by 400 ppm (22.2%) in M_{100} fuel and became 2200 ppm.

A similar situation is also valid for blended fuels containing 10% and 20% biodiesel by volume. As biodiesel ratio increased (10% and 20%) in blended fuels (with or without EHN additives) containing the same proportion of butanol or pentanol by volume, the average CO emission values of the combustibles in all cycles decreased between 0.3% and 3.8%. This result is similar to the work of Acaroğlu and Köse (2020); Yeşilyurt et al. (2018).

When the CO emission values of the blended fuels containing diesel, biodiesel, and alcohol in the same proportion by volume were compared, it was determined that the CO emission values of the blended fuels containing butanol were higher than the fuels containing pentanol. For example, while the CO emission value of $M_{60}B_{20}BU_{20}$ blended fuel containing 5% butanol at 1300 min^{-1} engine speed was 2000 ppm, this value was realized as 1800 ppm with a 10% decrease combustible containing pentanol ($M_{60}B_{20}P_{20}$) instead of butanol, which has the same ratios. İleri (2016) reported that the average CO emission values of $D_{70}S_{20}B_{10}$ and $D_{70}S_{20}P_{10}$ fuels increased by 20.35% and 8.76%, respectively, compared to diesel fuel.

When the average of all cycles examined, CO emissions decreased between 5.5% and 9.1% with the increase of alcohol content in all blended fuels containing both butanol and pentanol (with or without EHN additive). Similar results were also reported by Tüccar et al. (2014); Yeşilyurt et al. (2018). Higher viscosity and density result in weaker atomization and poor fuel distribution in the combustion chamber, resulting in incomplete combustion and higher CO formation (İleri, 2016).

The addition of EHN additives to the fuels slightly increases the CO emission values. Atmanlı (2016b); İleri (2016); Imdadul et al. (2016a) is similar to the studies. When EHN is added, HO_2 and H_2O_2 levels decrease and negatively affect OH and CO oxidation. 2-ethylhexyl nitrate (EHN) also causes increased diffusion combustion mixture with locally high equivalence ratios (Rashed et al., 2016)

3.2.2 Change of carbon dioxide (CO_2) values

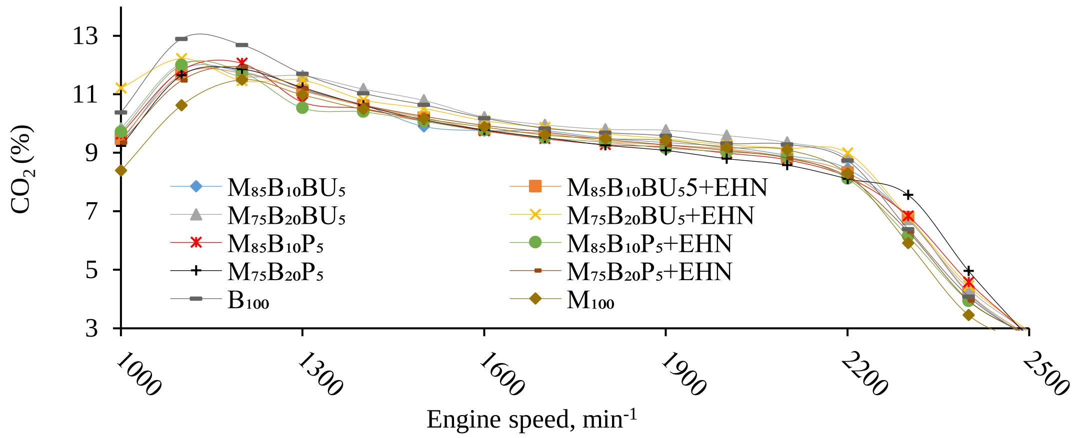


Figure 5. Change in carbon dioxide (CO_2) emission values of M_{100}, B_{100}, and mixed fuels (containing 5% BU or P) depending on engine speed

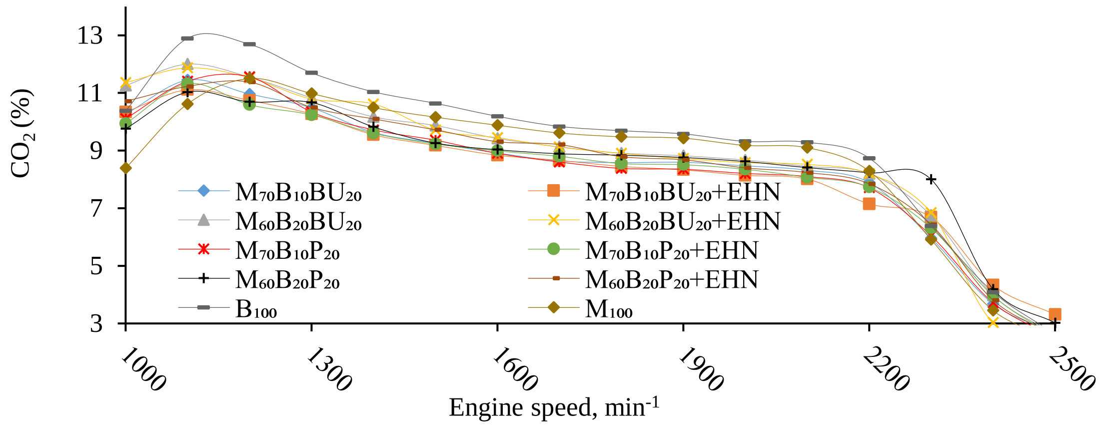


Figure 6. Change in carbon dioxide (CO_2) emission values of M_{100}, B_{100}, and mixed fuels (containing 10% BU or P) depending on engine speed

The variation of CO_2 emission values of diesel (M_{100}), biodiesel (B_{100}), and blended fuels (EHN added – non-additive) in exhaust emission tests performed under full load conditions depending on engine revolution speed (min^{-1}) given in *Figures 5*, *6* and *7*.

CO_2 emissions of all test fuels decreased with increasing engine speed. As the engine speed increases, the air movements and turbulence in the cylinder increase. Thus, it is easier for the fuel injected into the cylinder to form a mixture with the air. Alcohol blends reduced the viscosity of diesel fuel and provided better pulverization of the blend fuel (Yapmaz et al., 2021)

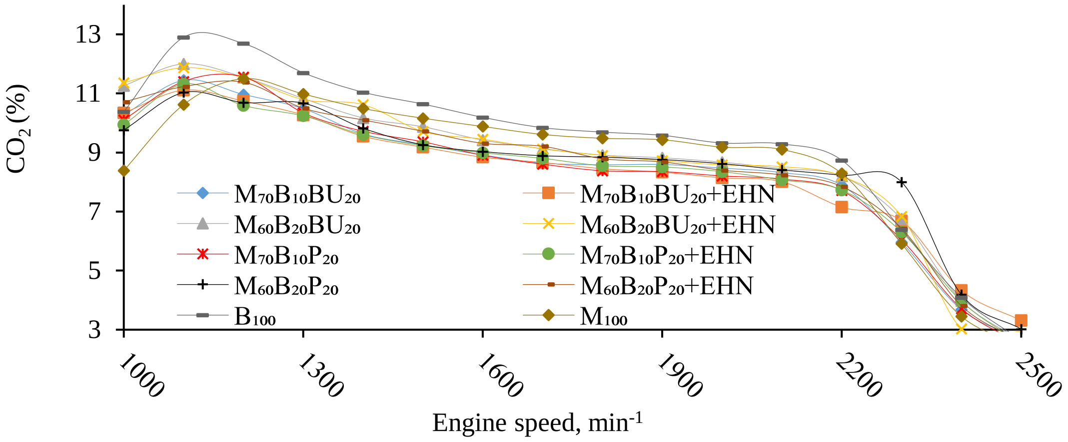


Figure 7. Change in carbon dioxide (CO_2) emission values of M_{100}, B_{100}, and mixed fuels (containing 20% BU or P) depending on engine speed

As a result of the comparison of the values of diesel (M_{100}) and safflower biodiesel (B_{100}) fuels, the CO_2 emission values of M_{100} fuel showed lower values than B_{100} were determined that at all engine speeds. While the CO_2 emission value of the B_{100} fuel was 11.7% at 1300 min^{-1} engine speed at which the maximum engine torque has obtained, this value has determined as 10.98% in the M_{100} fuel. Nanthagopal et al. (2018); Tillem (2005) reported that CO_2 emission values of biodiesel are higher than diesel fuel. In the study of Acaroğlu and Köse (2020), they stated that biodiesel fuel (B100) and mixtures (B5 and B7) contribute to combustion since the amount of oxygen is higher than diesel fuel (D100) and the density of biodiesel is higher of than diesel fuel, the total fuel mass increases, the CO_2 emission values are slightly higher. A similar situation is also valid for blended fuels containing 10% and 20% biodiesel by volume. As the biodiesel ratio increases (from 10% to 20%) in the blended fuels containing the same proportion of butanol or pentanol by volume, the average CO_2 emission values of the combustibles in all cycles increased between 0.2% and 5%. This result is similar to Şahin and Öğüt (2018); Yeşilyurt et al. (2018) studies. When the CO_2 emission values of blended fuels containing diesel, biodiesel, and alcohol (butanol or pentanol) at the same volume by volume are compared, the CO_2 emission values of blended fuels containing butanol are higher than fuels containing pentanol. For example, while the CO_2 emission value of the $M_{60}B_{20}BU_{20}$ blended fuel containing 20% butanol at 1300 min^{-1} engine speed was 10.83%, this value decreased slightly to 10.54% in the same combustible containing pentanol instead of butanol ($M_{60}B_{20}P_{20}$).

According to the results of the research, the CO_2 emission of the blended fuels gave similar results to the M_{100} fuel, and a decrease was observed in the emission values when compared to the B_{100} fuel. The reduction in CO_2 emissions for blend fuels may be due to oxygen content and hydrogen molecules in the fuel structures.

CO_2 emissions decreased with an increase of alcohol content (5, 10, and 20 %) in all blended fuels containing both butanol and pentanol. Similar results have also been reported by Lujaji et al. (2011); Yeşilyurt et al. (2018). Since there are fewer carbon atoms in the structure of high alcohols than diesel fuel, the CO_2 emission decreased between 3.7% and 6.9% when the average of all cycles was taken as the alcohol content in the mixtures increased. It has been observed that there is a decrease in CO_2 emissions with the use of EHN additive in fuel mixtures.

3.2.3 Comparison of oxygen (O2) emission values

The variation of O_2 emission values of diesel (M_{100}), biodiesel (B_{100}), and blended fuels (EHN added – non-additive) in exhaust emission tests performed under full load conditions depending on engine revolution speed (min^{-1}) given in *Figures 8, 9* and *10*.

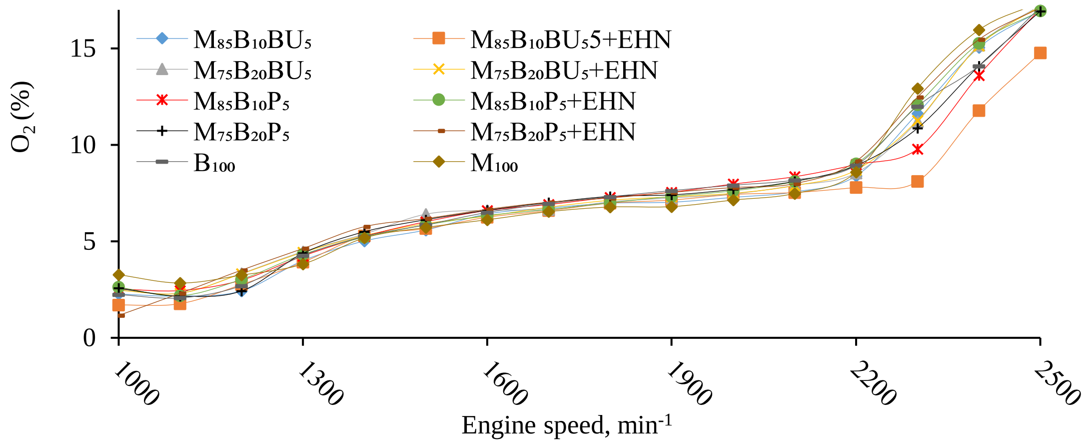


Figure 8. Change in oxygen (O_2) emission values of M_{100}, B_{100}, and mixed fuels (containing 5% BU or P) depending on engine speed

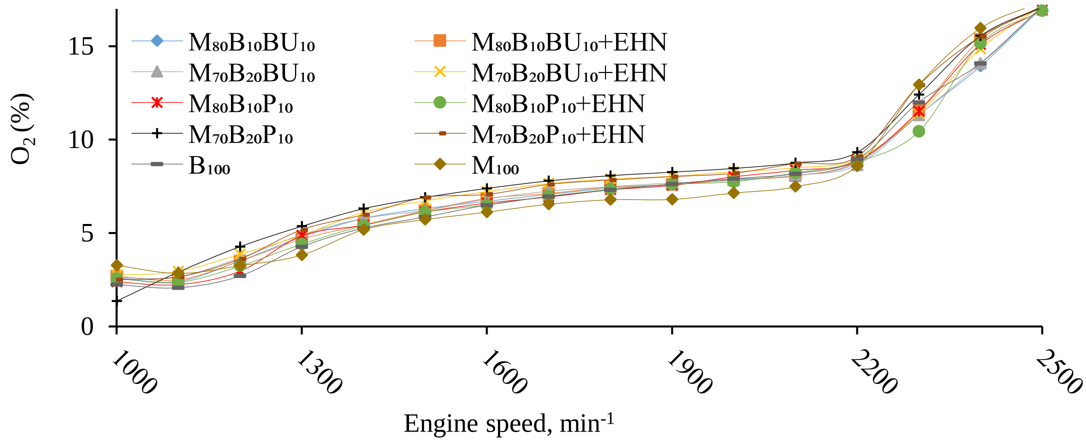


Figure 9. Change in oxygen (O_2) emission values of M_{100}, B_{100}, and mixed fuels (containing 10% BU or P) depending on engine speed

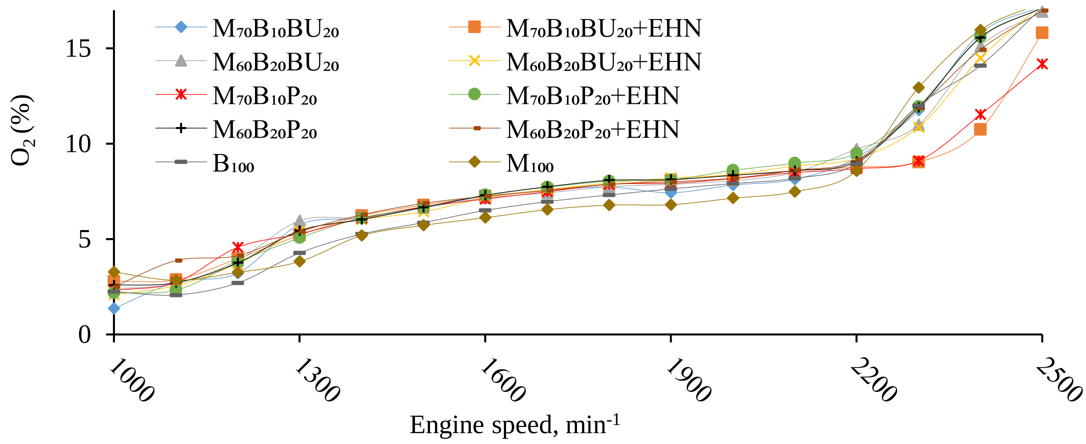


Figure 10. Change in oxygen (O_2) emission values of M_{100}, B_{100}, and mixed fuels (containing 20% BU or P) depending on engine speed

As a result of the comparison of the values of diesel (M_{100}) and safflower biodiesel (B_{100}) fuels, the O_2 emission values of M_{100} fuel showed lower values than B_{100} were determined that at all engine speeds. While the O_2 emission value of the B_{100} fuel was 4.27% at 1300 min^{-1} engine speed at which the maximum engine torque has obtained, this value has determined as %3.82 in the M_{100} fuel. Aydın et al. (2012); Tillem (2005); Yeşilyurt et al. (2018)

stated that the least O_2 emission value among all fuels and mixtures was obtained from standard diesel fuel (M_{100}). Ağbulut et al. (2019) also reported that diesel fuel causes the lowest O_2 emission since there is no oxygen in its molecular content. A similar situation is also valid for blended fuels containing 10% and 20% biodiesel by volume. As the biodiesel ratio increases (from 10% to 20%) in the blended fuels containing the same proportion of butanol or pentanol by volume, the average O_2 emission values of the combustibles in all cycles increased between 0.3% and 12.8%. This result is similar to Yeşilyurt et al. (2018) studies.

O_2 Emissions of all test fuels increased with increasing engine speed (especially between 2200 rpm and 2500 rpm). The reasons for this increase in O_2 emission are the decrease in the time allocated for combustion at high speeds and the insufficient amount of oxygen to react (Yüksel et al., 2019).

When the O_2 emission values of blended fuels containing diesel, biodiesel, and alcohol (butanol or pentanol) at the same volume by volume are compared, the O_2 emission values of blended fuels containing butanol are relatively lower than fuels containing pentanol. For example, while the O_2 emission value of the $M_{60}B_{20}BU_{20}$ blended fuel containing 20% butanol at 1300 min^{-1} engine speed was 5.96%, this value decreased slightly to 5.44% in the same combustible containing pentanol instead of butanol ($M_{60}B_{20}P_{20}$). Yeşilyurt et al. (2018) also found a similar relationship in their studies. O_2 emissions decreased with an increase of alcohol content (5, 10, and 20 %) in all blended fuels containing both butanol and pentanol. Similar results have also been reported by Yeşilyurt et al. (2018). In general, it has been determined that O_2 emissions are reduced somewhat by adding EHN additives to blended fuels.

3.2.4 Comparison of nitrogen oxide (NOx) emission values

The variation of NO_x emission values of diesel (M_{100}), biodiesel (B_{100}), and blended fuels (EHN added – non-additive) in exhaust emission tests performed under full load conditions depending on engine revolution speed (min^{-1}) given in *Figures 11, 12* and *13*.

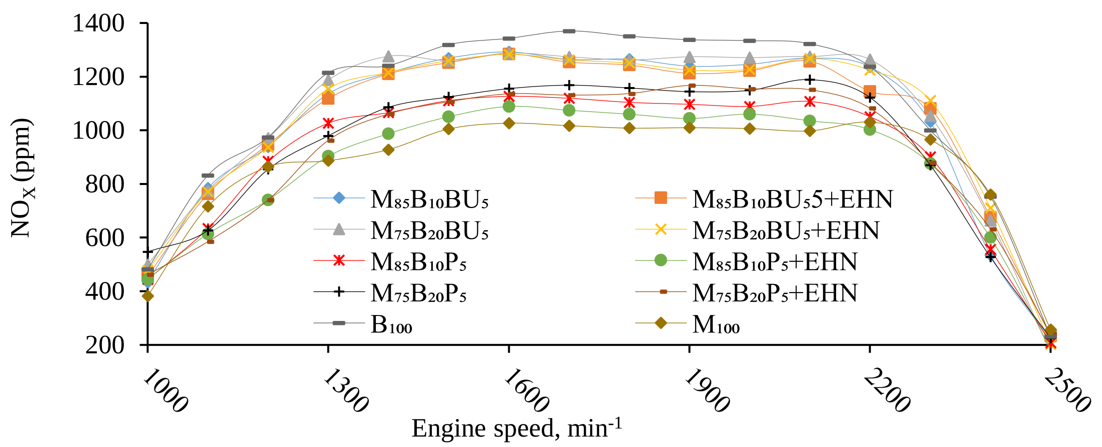


Figure 11. Change in nitrogen oxide (NO_x) emission values of M_{100}, B_{100}, and mixed fuels (containing 5% BU or P) depending on engine speed

As a result of the comparison of the values of diesel (M_{100}) and safflower biodiesel (B_{100}) fuels, the NO_x emission values of M_{100} fuel showed lower values than B_{100} were determined that at all engine speeds. While the O_2 emission value of the B_{100} fuel was 1214 ppm at 1300 min^{-1} engine speed at which the maximum engine torque has obtained, this value has determined as 886 ppm in the M_{100} fuel. The reason why the NO_x emission value is higher in B_{100} fuel compared to diesel is the higher oxygen content it contains. Altun (2010); Tillem (2005) reported in their studies that the combustion temperature of biodiesel fuels increases as a result of containing more oxygen than diesel fuel, and this causes an increase in NO_x emissions due to the high amount of oxygen that can be oxidized with nitrogen in the environment.

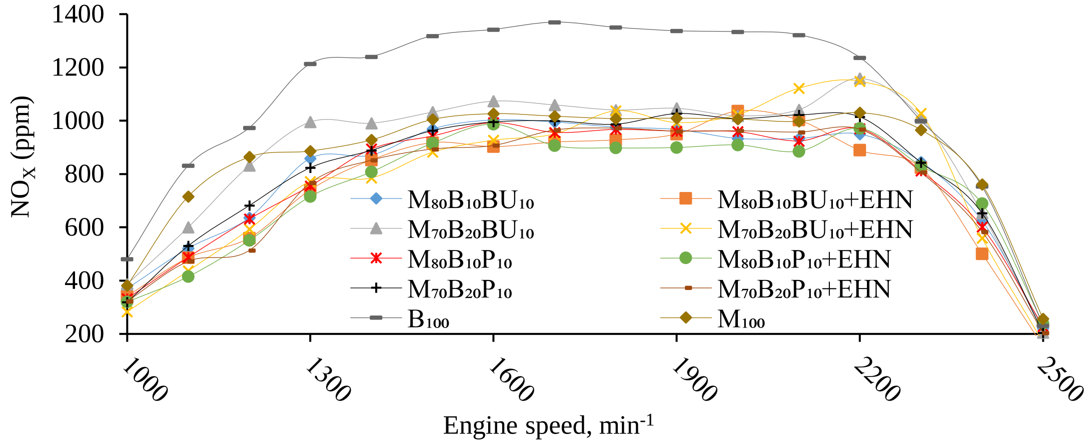


Figure 12. Change in nitrogen oxide (NO_x) emission values of M_{100}, B_{100}, and mixed fuels (containing 10% BU or P) depending on engine speed

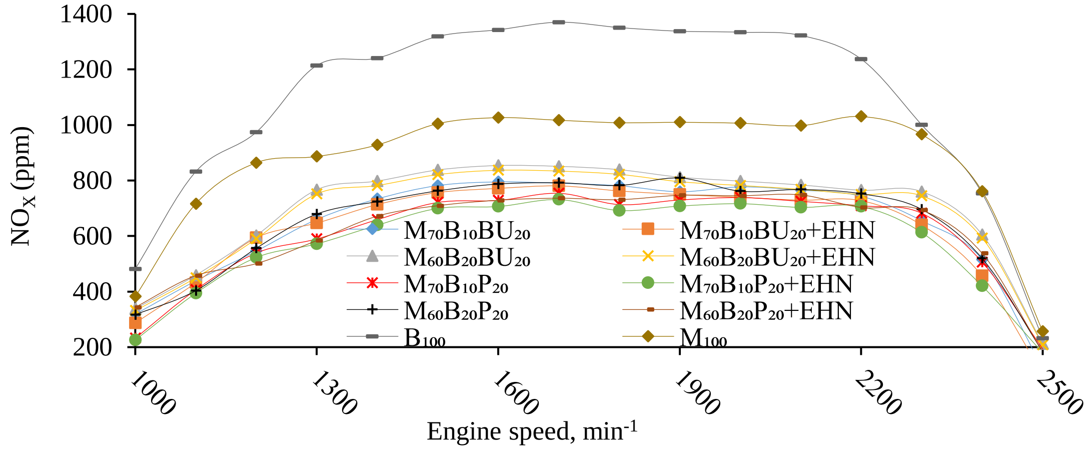


Figure 13. Change in nitrogen oxide (NO_x) emission values of M_{100}, B_{100}, and mixed fuels (containing 20% BU or P) depending on engine speed

A similar situation is also valid for blended fuels containing 10% and 20% biodiesel by volume. As the biodiesel ratio increases (from 10% to 20%) in the blended fuels containing the same proportion of butanol or pentanol by volume, the average NO_x emission values of the combustibles in all cycles increased between 1.3% and 11.6%. This result is similar to Manu and Mahla (2014); Reşitoğlu (2010) studies.

It has been observed that the use of butanol and pentanol in blended fuels reduces NO_x emissions compared to diesel fuel. Yeşilyurt (2020) found that fuels containing alcohol have lower NO_x emissions than diesel fuel. Altun (2010) reported that reductions in NO_x emissions were detected in blended fuels containing high percentages of alcohol (10-20%) compared to diesel fuel, and that the cooling effect, combustion temperature and NO_x emissions were reduced due to the low calorific value and high evaporation heat of alcohol fuels.

When the NO_x emission values of blended fuels containing diesel, biodiesel, and alcohol (butanol or pentanol) at the same volume by volume are compared, the NO_x emission values of blended fuels containing butanol are relatively lower than fuels containing pentanol. For example, while the NO_x emission value of the $M_{60}B_{20}BU_{20}$ blended fuel containing 20% butanol at 1300 min^{-1} engine speed was 767 ppm this value decreased slightly to 679 ppm in the same combustible containing pentanol instead of butanol ($M_{60}B_{20}P_{20}$). Atmanlı (2016a); Nanthagopal et al. (2018) also found a similar relationship in their studies.

When the average of all cycles examined, NO_x emissions decreased between 30% and 40% with the increase of alcohol content in all blended fuels containing both butanol and pentanol (with or without EHN additive).

Similar results found by Manu and Mahla (2014); Yilmaz et al. (2014) also have been reported in their study. The addition of EHN additives to the fuels slightly decreases the NO_X emission values. Similar results were also reported by Atmanlı (2016b). Although nitrogen molecules in the chemical structure of EHN accelerate NO production, increasing the cetane number shortens the duration of the premixed combustion phase, increasing the ignition delay and reducing the ignition delay. As a result, the combustion temperature and thermal NO_X are reduced. Also, the increase in the cetane number accelerates the generation of free radicals, which promotes the formation of free radicals, which can remove hydrogen atoms from mixtures that restrict the oxidation of hydrocarbon and nitrogen atoms, thus reducing NO_X (Imdadul et al., 2016b).

3.2.5 Comparison of hydrocarbon (HC) emission values

The variation of HC emission values of diesel (M_{100}), biodiesel (B_{100}), and blended fuels (EHN added – non-additive) in exhaust emission tests performed under full load conditions depending on engine revolution speed (min^{-1}) given in *Figures 14, 15* and *16*.

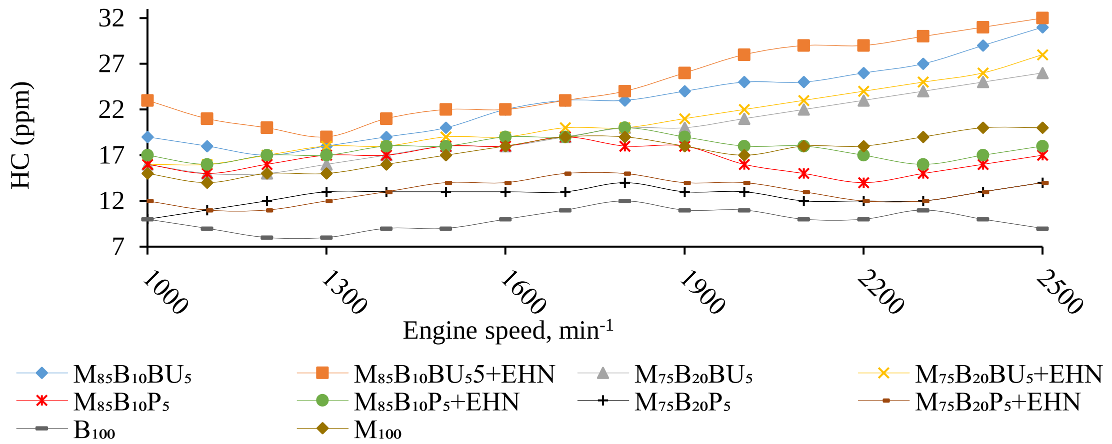


Figure 14. Change in hydrocarbon (HC) emission values of M_{100}, B_{100}, and mixed fuels (containing 5% BU or P) depending on engine speed

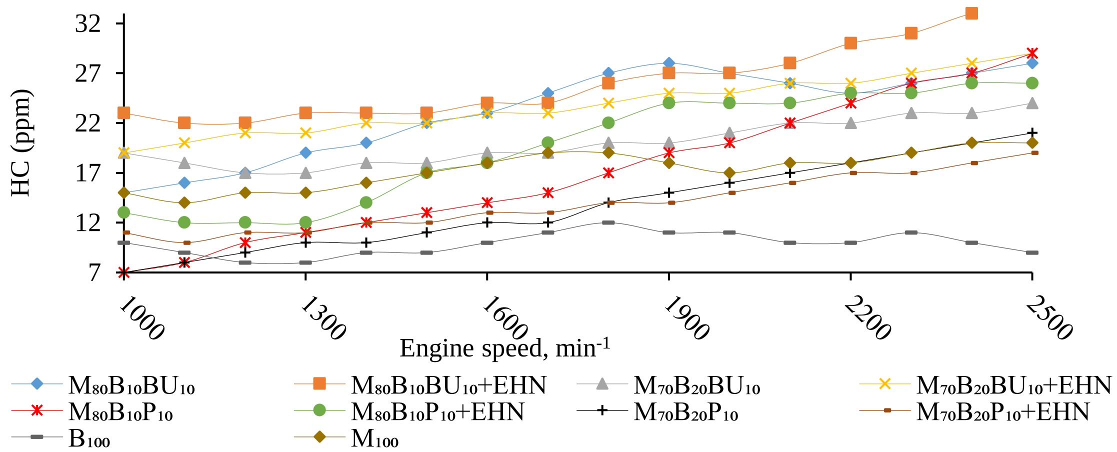


Figure 15. Change in hydrocarbon (HC) emission values of M_{100}, B_{100}, and mixed fuels (containing 10% BU or P) depending on engine speed

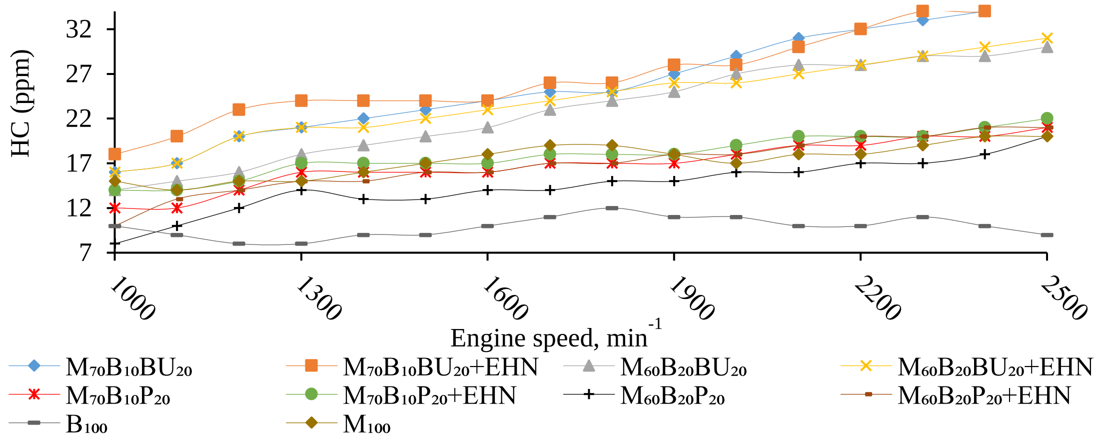


Figure 16. Change in hydrocarbon (HC) emission values of M_{100}, B_{100}, and mixed fuels (containing 20% BU or P) depending on engine speed

As a result of the comparison of the values of diesel (M_{100}) and safflower biodiesel (B_{100}) fuels, the HC emission values of M_{100} fuel showed higher values than B_{100} were determined that at all engine speeds. While the HC emission value of the B_{100} fuel was 8 ppm at 1300 min^{-1} engine speed at which the maximum engine torque has obtained, this value has determined as 14 ppm in the M_{100} fuel. Since diesel (M_{100}) does not contain oxygen in its molecular content, HC emissions are higher than B_{100} fuel. Similar results were also reported by Aydın et al. (2012); Rajasekar (2016).

A similar situation is also valid for blended fuels containing 10% and 20% biodiesel by volume. As the biodiesel ratio increases (from 10% to 20%) in the blended fuels containing the same proportion of butanol or pentanol by volume, the average HC emission values of the combustibles in all cycles decreased between 6% and 29%. Imdadul et al. (2016b) also obtained similar results in the study.

When the HC emission values of blended fuels containing diesel, biodiesel, and alcohol (butanol or pentanol) at the same volume by volume are compared, the HC emission values of blended fuels containing butanol are relatively higher than fuels containing pentanol. For example, while the HC emission value of the $M_{60}B_{20}BU_{20}$ blended fuel containing 20% butanol at 1300 min^{-1} engine speed was 14 ppm this value increased to 18 ppm in the same combustible containing pentanol instead of butanol ($M_{60}B_{20}P_{20}$). While the average HC values of butanol-containing blended fuels (with and without EHN additives) increased up to 55% compared to M_{100} fuel, it was determined that fuels containing pentanol were at low or very close values. It is also seen in the study conducted by Atmanlı (2016a) that fuels containing butanol increase HC emissions more than fuels containing pentanol.

When the average of all cycles examined, HC emissions decreased between 1% and 29% with the increase of alcohol content in all blended fuels containing both butanol and pentanol (with or without EHN additive). This can be explained by the low cetane number and high evaporation temperature of alcohols. Since the low cetane number and high heat of evaporation cause the ignition delay and shortening of the combustion time, complete combustion cannot take place, and as a result, HC emission occurs. Yilmaz et al. (2014) reported that an increase in butonal ratio by volume increases HC emission, Imdadul et al. (2016b) reported that an increase in pentanol by volume increases HC emission. Similar relationships were found by Kumar and Saravanan (2016); Nanthagopal et al. (2018); Rajasekar (2016); Zhu et al. (2016) and suggested the use of high alcohols at low rates to improve emissions.

When the averages of the fuel mixtures in all cycles are examined, the HC emissions of the blend fuels with the addition of EHN increased compared to the blend fuels without the addition of EHN. The addition of EHN to the mixtures increases the cooling effect in the cylinder, which leads to high HC emissions. In addition, this increase is due to the decrease in oxidative free radical formation. EHN helps increase the cetane number of the mixture, but also shortens the time available for the fuel-air mixture (Imdadul et al., 2016b); Imdadul et al. (2017)) reported that the addition of EHN to pentanol fuel mixtures increased the HC emission values.

4. Conclusions

The lowest average CO emission value was obtained in B_{100} with 4012 ppm, and in $M_{60}B_{20}P_{20}$ fuel with 4056 ppm from blended fuels. The highest CO emission value was found in M_{100} fuel with 5293 ppm, and the highest value in $M_{85}B_{10}BU_5$+EHN combustible with 4850 ppm among blended combustibles.

The lowest average CO_2 emission value of 8.23% was found in $M_{70}B_{10}P_{20}$+EHN fuel. The fuel that gave the highest CO_2 emission value was B_{100} with 9.32%, and $M_{75}B_{20}BU_5$ combustible with 9.29% in blended fuels.

• The lowest average HC emission value was found 9.9 ppm in B_{100} fuel and 12.6 ppm in $M_{75}B_{20}P_5$ fuel from blended fuels. The highest HC emission was obtained from $M_{70}B_{10}BU_{20}$+EHN combustible with a value of 26.9 ppm.

• The lowest average O_2 emission value of 6.59% was found in $M_{85}B_{10}BU_5$+EHN fuel, and the highest O_2 emission value was determined in $M_{60}B_{20}P_{20}$+EHN fuel with 8.09%.

• The lowest average NOx emission was determined at 576 ppm in $M_{70}B_{10}P_{20}$+EHN fuel. The highest value obtained from B_{100} with 1089 ppm, and $M_{75}B_{20}BU_5$ with 1047 ppm among mixed fuels.

It has been determined that the 2-Ethylhexyl Nitrate additive, which is used as an additive in the mixtures, has positive effects on improving emissions.

Funding Information

This research was supported by a grant from Center of Scientific Research Project of Selçuk University (BAP Project Number: 18101007).

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