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Investigation of the usability of essential oils in diesel engines as a new biodiesel source

Yeni bir biyodizel kaynağı olarak uçucu yağların dizel motorlarda kullanılabilirliğinin araştırılması

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Abstract
This article has focused on essential oils as alternative fuels and fuel additives. The essential oil is obtained from Salvia Candidissima plant. While a Clevenger type apparatus was used to determine the oil yield of Salvia Candidissima plant, a retort was produced for the bulk oil to be used in the experiments. The compounds of the obtained oil were determined by Gas chromatography / Mass spectrometry (GC / MS) and the essential oil was converted into biofuel. The produced biofuel was added 5% by volume to the reference diesel fuel (DF) and mixed fuel (SB-5) was formed. Later, SB-5 and DF fuels were tested at 1500 fixed cycles and different loads, and emission and combustion data were obtained. As a result of the experiment, effective decreases in Carbon Monoxide (CO) and Hydrocarbon (HC) emissions and increases in NOx emissions were observed with SB-5 fuel mixture. In addition, higher combustion data were obtained with SB-5 fuel mixture than DF fuel.

Keywords: Biofuels, Essential oils, Diesel engines, Emission and combustion

Öz
Bu makale, alternatif yakıt ve yakıt katkı maddesi olarak uçucu yağlar üzerine yoğunlaşmıştır. Uçucu yağ Salvia Candidissima, bitkisinden elde edilmiştir. Salvia Candidissima, bitkisinin yağ verimini belirlemek için Clevenger tipi bir aparat kullanılırken, deneylerde kullanılacak kütlesel yağ için imbik imal edilmiştir. Elde edilen yağın bileşikleri Gaz kromatografisi / Kütle spektrometresi (GC / MS) ile belirlenmiş ve uçucu yağ biyoyakıta dönüştürülmüştür. Üretilen biyoyakıt referans dizel yakıtına (DF) hacimsel olarak % 5 ilave edilmiş ve karışım yakıt (SB-5) oluşturulmuştur. Daha sonra, SB-5 ve DF yakıtları 1500 sabit devirde ve farklı yüklerde test edilmiş, emisyon ve yanma verileri alınmıştır. Deney sonucunda SB-5 karışım yakıtı ile Karbonmonoksit (CO) ve Hidrokarbon (HC) emisyonlarında etkili düşüşler, NOx emisyonlarında artışlar gözlemlenmiştir. Ayrıca SB-5 yakıt karışımı ile DF yakıtından daha yüksek yanma verileri elde edilmiştir.

***Anahtar kelimeler**: Biyoyakıtlar, Uçucu yağlar, Dizel motorlar, Emisyon ve yanma*

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1. Introduction

For humanity, energy is one of the indispensable components. This constitutes the base for economic growth. As the rate of the world population rises with each passing year, energy demand increases (Qiul ance et al., 2011). Fossil fuels account for about 87 per cent of the energy resources used.70 percent of the fossil fuel reserves are coal, 14 percent oil, 14 percent natural gas and 2 percent other fossil resources (BP, 2008). The storage quantity of current reserves will decrease dramatically within an average of 100 years, according to the study carried out in conjunction with the consumption rates of fossil resources. Furthermore, taking into account the CO_2 emissions of fossil fuels, environmental pollution is expected to rise by 50 per cent in 2030 (Stigka et al., 2014). The rapid decline in oil resources in recent years, the steady increase in oil prices and the use of fossil fuels Adverse environmental impacts induced by the quest for energy have been geared towards renewable sources of energy. In the study and production of renewable energy sources, various approaches have been used. Renewable "Biomass Energy" is of significant importance among these approaches. Materials of animal and plant origin are in the class of biomass energy resources (Kralova and Sjöblom, 2010). An alternative fuel derived from oils of vegetable or animal origin is biodiesel, which is the sub-subject of biomass energy within renewable energy sources. It is simpler to generate biodiesel fuel than other renewable sources of energy (such as wind and solar energy). Its production is becoming widespread day by day because of its low cost. Furthermore, biodiesel, a sustainable energy form, creates new business areas, particularly in rural areas, by enabling industry, agriculture and the environment to cooperate (Atabani et al., 2013). However, 81% of biodiesel was obtained from vegetable oils (Oecd/Fao, 2016). Among the vegetable oils, oilseeds such as canola (rapeseed), sunflower, soybean, safflower, cotton, palm and jatropa are the most used. This situation enables the allocation of agricultural lands to oilseed crops and causes global food price increase, high water consumption and biodiversity loss. Therefore, in the search for new and renewable biodiesel resources, natural and self-growing plants have been studied. Among these, salvia plant species stand out. Salvia species are wild perennial plants that are highly resistant to hot and dry conditions and contain essential oil. Hoseini et al., (2017) explained in their study that the high oxygen content of biodiesel obtained from the Salvia macrosiphon plant provides significant general improvements in the combustion reaction, especially in B20 (20% biodiesel by volume and 80% diesel fuel by volume). On the other hand, Gholami et al., (2019) investigated the biodiesel potential of Salvia leriifolia plant in their study. Salvia leriifolia stated that it can grow in harsh climatic conditions and poor quality soils due to its high salt and drought tolerance and therefore it is an ideal biodiesel production source in all countries facing water scarcity and low fertile soil problems. In this study, Candidissima was investigated in Salvia species. Salvia Candidissima is a natural species that grows spontaneously even in areas not suitable for agricultural activities. It grows widely in our country.

2. Meterial method

2.1. The composition of essential oils

Essential oils are found in many parts of the plant and rarely in their stems and shells. 90% of the compounds found in essential oils are terpenoid compounds (Tisserand and Young, 2014; Başaran, 2003; September, 2011). Other compounds are phenolcarbonic acids, phenylpropane derivatives, sulfur-containing compounds, unbranched hydrocarbides and derivatives, simple phenols and ethers, short-chain fatty acids and nitrogenous compounds (Tisserand and Young, 2014). Terpenes; The essential oil contains alcohol, ester, oxide, aldehyde, ketone and ether. These are grouped as acyclic, monocyclic or bicyclic (Antunes, 2004). The general chemical formula of many natural terpenoid hydrocarbons is $(C_5H_8)n$. The classification related to the C number or n value (number of bound isoprene units) is as shown in Table 1. Each class in the table is divided into subgroups according to the number of rings in the structure. While monoterpenoid acyclic terpenoids are non-ring structures, monocyclic terpenoids are one-ring and bicyclic terpenoids are two-ring structures. Many terpenoids are colorless, fragrant, lighter than water, but there are also those in solid form such as camphor. They are all soluble in organic solvents and are generally insoluble in water. Most are optically active. Terpenoids are the most important group in essential oil composition. When the literature is analyzed, although the researchers have addressed terpenes in the first studies on the subject, this group is now called monoterpenoid hydrocarbons. Essential oils contain many chemical structures. For example, limonene, linalol and pinens are found in many essential oils. However, it has been observed that each essential oil is dominated by different components. It has been reported that the essential oil content of even the same plants varies (Akgül, 2011; Schulz et al., 2003; Çelik et al., 2014). Volatile compounds, which contain the quality of essential oil, determine. In the composition of an essential oil, sometimes there may be hundreds of large and small compounds. These compounds can be identified by being separated from each other by an advanced technique called Gas Chromatography / Mass Spectrometry (G_C / M_S).

Table 1. Terpenoid classification

Catomic number	n value	Terpenoid class
5	1	Hemiterpenoidler (C_5H_8)
10	2	Monoterpenoidler ($C_{10}H_{16}$)
15	3	Seskiterpenoidler ($C_{15}H_{24}$)
20	4	Diterpenoidler ($C_{20}H_{32}$)
25	5	Sesteterpenoidler ($C_{25}H_{40}$)
30	6	Troterpenoidler ($C_{30}H_{48}$)
40	8	Tetraterpenoidler ($C_{40}H_{64}$)
>40	>8	Politerpenoidler (C_5H_8)n

2.2. Properties of essential oils

1. Essential oils are usually liquid at room temperature.
2. The stain left when it is dropped on the paper is not permanent as in fixed oils, it will disappear over time.
3. Essential oil is mostly colorless when distilled.
4. Essential oils are resinized with long-term storage, light and oxygen effects.
5. Its specific weight ranges from 0.84 to 1.18.
6. The boiling points of essential oils are high (150-300 °C).
7. Essential oils have low water solubility (1: 200 or less).
8. Essential oils are optically active.
9. The specific degree of refraction may vary even at essential oils from the same plant at different times.

The composition of essential oils can vary in proportion (Özler et al., 2009; Qudah et al., 2014) Table 2. Compared with other biodiesel sources of essential oil in terms of density and viscosity values.

Table 2. Comparison of density and viscosity values (Akader, 2006; Ilkılıc and Öner, 2017).

Name of vegetable oil	Specific mass (g / ml)	Kinematic viscosity (mm^2 / s)
Diesel fuel	0.86	2.9
Sunflower oil	0.92	34.9
Soy oil	0.92	36.4
Cotton oil	0.91	37.4
Peanut	0.91	37.2
Rapeseed oil	0.92	39.0
Flax oil	0.92	27.2
Sesame oil	0.91	35.5
Salvia Candidissimada	0.90	2.17

2.3. Essential oil plant

Salvia Candidissima (Figure 1. /Taxon Page) is one of the important essential oil families, Lamiaceae. It is stated that the approximate number of species is 1000 (Bayram, 2001). There are 95 species in Turkey (İpek et al., 2012). 51 of them are endemic (Özler et al., 2009). Usually, Greece, Iraq, Iran and Turkey are in some regions (Qudah et al., 2014). It is a perennial shrub in the form of a perpendicular trunk 30-60 cm tall, branching from the top (Alizadeh, 2013). It is found in rocky limestone and schist slopes. It generally grows at an altitude of 700-2000 m.

Figure 1. Salvia Candidissima

Table 3. Taxon page (Tubives, 2020).

Family	**Lamiaceae**	
Genus	*Salvia L.*	
Taxon	*Salvia candidissima VAHL subsp. occidentalis HEDGE*	
Taxonomic Hierarchy		
Kingdom Plantae		
Subkingdom Tracheobionta		
Division Magnoliophyta		
Class Magnoliopsida		
Class Magnoliopsida		
Subclass Asteridae		
Order Lamiales		
Family Lamiaceae		
Family Lamiaceae		
Genus *Salvia*		
Species Salvia candidissima VAHL		
General Taxon Information		
Life		*: perennial*
Structure		*: Weed*
Life Form		*:*
Blooming		*: 5-9*
Habitat		*: Rocky volcanic and limestone rocks, chalk hills, field edges*
Endemik		*: Not endemic*
Element		*: İran-Turan*
Turkey Distribution		*: Terrestrial and West. Anatolia*
General Distribution		*: Greece, Albania*

2.4. Essential oil production by hydrodistillation

Essential oil was made from the study plant by hydro distillation method. A retort working with this method was manufactured. (Figure 2,). With this method, the oil extraction steps are first put into the retort after the plant mass is cleaned and sorted. In the retort cauldron, water and plant mass are boiled together. The water evaporates and carries the oil molecules in the plant to the cooler. In the cooler, the fat molecules condense and separate from the water. The amount of essential oil obtained is expressed in volumes. Water distillation gives better results with fine particle materials (Edoq, 2000).

Figure 2. Steps of obtaining oil from plant biomass.

2.5. Essential oils G_C-M_S measurements

G_C-M_S is among the most important and common techniques for separating essential oils. The separation of the components depends on the polarity and volatility of the analytes. The principle of G_C is based on the differential partitioning of solutes between the mobile and stationary phase. It is a very simple, reliable method, and can be applied to separate volatile substances stable at temperatures up to 350-400 °C. If the sample or mixture is not volatile, the sample must be properly derivatized to make it volatile. G_C-M_S analysis was performed for component determination of essential oil. For this purpose, analysis was performed by diluting 100 µl essential oil with 5 ml hexane. The analysis of the essential oil components was carried out by Trace DSQ II (Thermo Fisher Scientific, Waltham, MA, USA) gas chromatography with flame ionization detector and autosampler. The separation was made in a 60 m long, 0.25 mm inner diameter, film thickness 0.25 µm Tg-wax column. The transport of the compounds in the column was achieved with helium (1 ml / min) gas. Oven temperature increased by 5 °C / min after being waited for 10 minutes at 40 °C and reached 240 °C at this temperature and 12 minutes at this temperature. It heated. The injection was carried out in split mode (1:20), at 250 °C, in a volume of 1 µl. Ion source temperature is 230 °C. Mass Spectrometry 35-350 m / z atomic mass units were carried out in the scanning range by electron impact ionization. Mass spectral comparisons were made using NIST 2005 and Wiley 9 mass spectrum libraries to identify the compounds. Analysis results were obtained in relative %. C8-C20 nalkan standards (Mix no. 04070, Sigma – Aldrich, St. Louis, MO, USA) were used to calculate the retention indices (RI) of the samples. Plant gas chromatography (Figure 3).

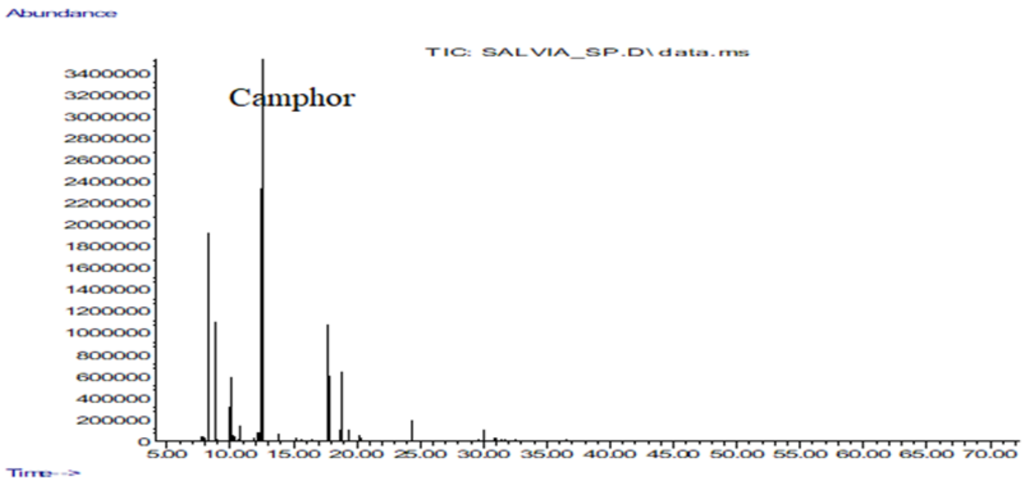


Figure 3. Gas chromatography (Main components of essential oil: camphor (28.94%), bornyl acetate (12.80%), borneole (9.44%), beta-cadinene (5.88%), alpha-caryophyllene (5.40%), 1.8-cineole (5.15%) (Çılğın, 2020)

2.6 Converting essential oil to fuel

Traditional production of biodiesel fuel; It is carried out by chemical transesterification, where short reaction time and high efficiency are obtained. Transesterification, also called alcohol-free, is the reaction of a fat or oil with an alcohol to form ester and glycerol (Figure 4,). In this reaction, more methanol and ethanol are preferred as alcohol due to their low cost, but propanol, butanol and amyl alcohol are also among the alcohols used (Fukuda et al., 2001). Transesterification reaction; It can usually be catalyzed by alkalis such as NaOH, KOH, acids such as sulfuric acid or lipase enzymes to increase the reaction rate and efficiency (Pizarro and Park, 2003). In this study, vegetable oil was heated up to 60 ° C in a magnetic heater. Then methanol-potassium hydroxide (KOH) mixture was added to the heated oil. The reaction took 2 hours.It was kept for an average of 48 hours for the completion of the transesterification reaction(İlkılıç at al., 2011).. After the waiting was over, glycerin and biodiesel formed. Since the glycerin phase density was greater than the biodiesel phase density, the glycerin phase was taken from the bottom of the settling vessel. The alcohol-to-oil molar ratio was 5: 1, the conversion of the product was 97.6%. The viscosity value, which was 2.17 mm^2 / s after transesterification, decreased by 7.96% to 2.01 mm^2 /s. Density value was 0.90 g/ml, while 1.12 % decrease was 0.89 g/ml. The resulting biodiesel was added 5% by volume to diesel fuel and the mixture fuel obtained was expressed as SB-B5.

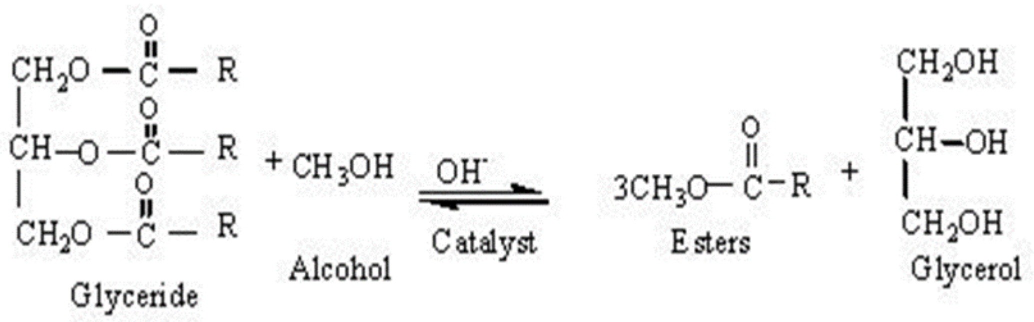


Figure 4. Transesterification of triglycerides with alcohols (Mutlubaş, 2016)

2.7. Experimental setup

Engine specifications used in the experiments Table.4 The device features used in the exhaust measurement are presented in Table.5 and the measurement device sensitivities are presented in Table.6.

Table 4. Specifications of the diesel engine.

Model	NWK22
Engine rated power @1500rpm	17kW
Engine cooling system	Water cooling
Intake system	Naturally aspirates
Engine model	4DW81-23D
Bore x stroke (mm)	85×100
Displacement (cm^3)	2400
Cylinder number	4
Combustion system	Direct injection
Compresion ratio	17:1
Injector nozzle number	4

Table 5. Technical specifications of the capelec cap 3200.

HC	0-20000 ppm	±1ppm
CO_2	0-20%	±0.1%
CO	0-15%	±0.001%
O_2	0-21.7%	±0.01%
NO_x	0-5000ppm	±1 ppm

Table 6. The accuracies of the measurements and uncertainties of test device

Engine parameter	Measurement range	Accuracy
Cylinder pressure sensor	0-200 bar	≤ ±0.5%
Engine speed	0-12000 rpm	± 0.1 % [o]
Fuel consumption	0.5-3000 g	± 0.5 g
HC	0-200000 ppm	± 1 ppm
CO_2	0-20 %	± 0.1 %
CO	0-15 %	± 0.001 %
O_2	0-21.7 %	± 0.01 %
NO_x	0-5000 ppm	± 1 ppm

3. Experiment results

3.1. Heat release relate

Figure 5 shows the heat release rate in the case of 7.04 kW load, Figure 6 shows the maximum heat release values of the experimental fuels in all load cases. Understanding the rate and process of heat release makes it easier for us to understand the internal combustion engine combustion process. When Figure 6 is examined, it is seen that the pre-ignition heat release values are below zero. Because the injected fuel takes heat from the environment and reduces the temperature of the environment in order to ignite before the ignition phase. At the end of the ignition delay period, the fuel burns suddenly and the heat release values are transferred to the positive area. As the volume expands at the end of the combustion process, the heat release rate gradually decreases. With the opening of the exhaust valves, the temperature drops suddenly and the heat release values are transferred back to the negative area. When Figures 5 and 6 are examined, values compatible with the general burning tendency appear. In each stage loading of SB-5 fuel, DF fuel values occurred later as crank angle but the peak values were higher.

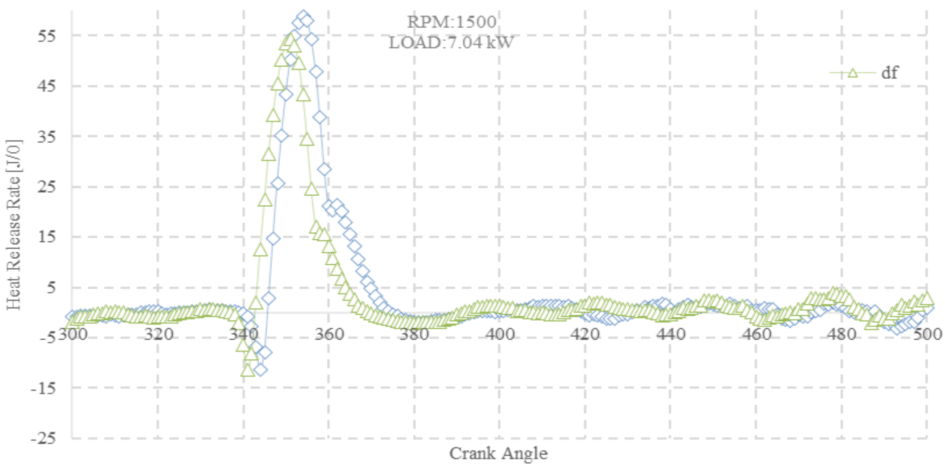


Figure 5. Changes in heat release values depending on the crank angle

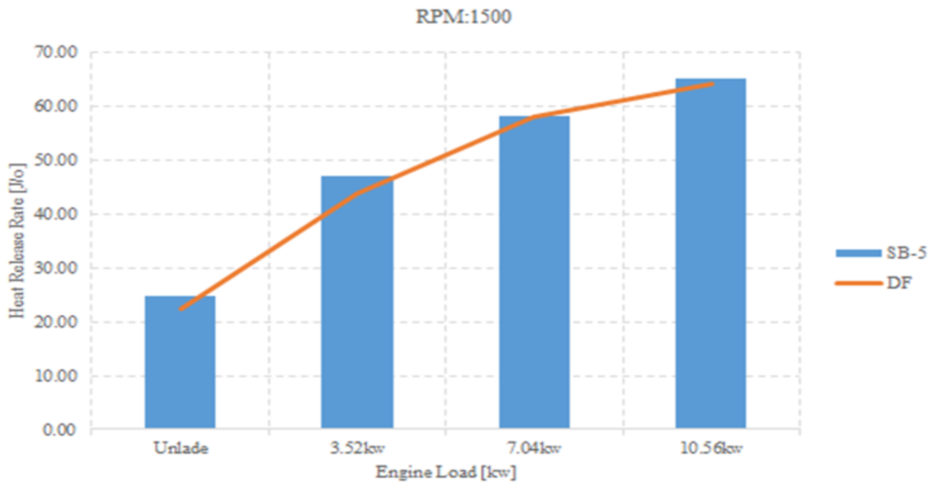


Figure 6. Maximum heat release changes depending on the crank angle

3.2.Average gas temperatures

Figure 7, shows average gas temperature values under 7.04 kW load, Figure 8, shows the maximum average gas temperature values of the experimental fuels in all load cases. When the average gas temperature values of the experimental fuels are examined It is seen that the average gas temperatures obtained with vegetable oil based SB-5 blended fuel are higher than the DF reference diesel fuel. The higher oxygen concentration in the vegetable oil content compared to the DF reference fuel resulted in higher average gas temperatures (Sezer, 2016).

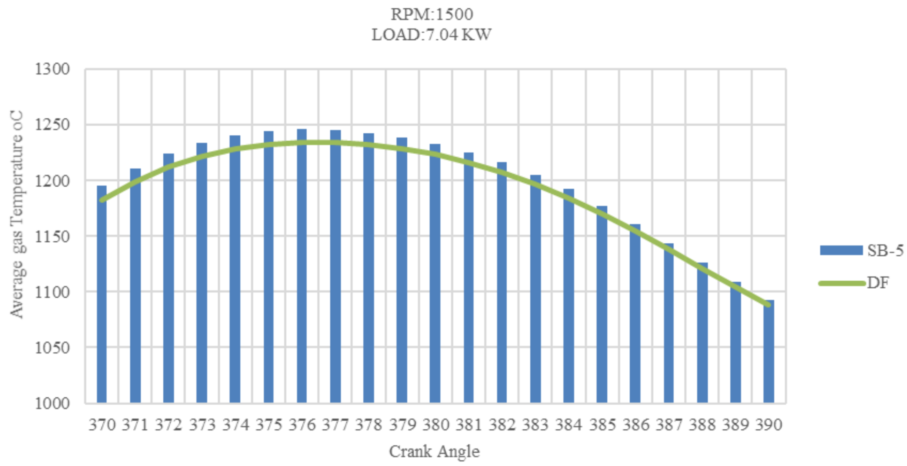


Figure 7. changes of gas temperature values depending on the crank angle [7.04 kw]

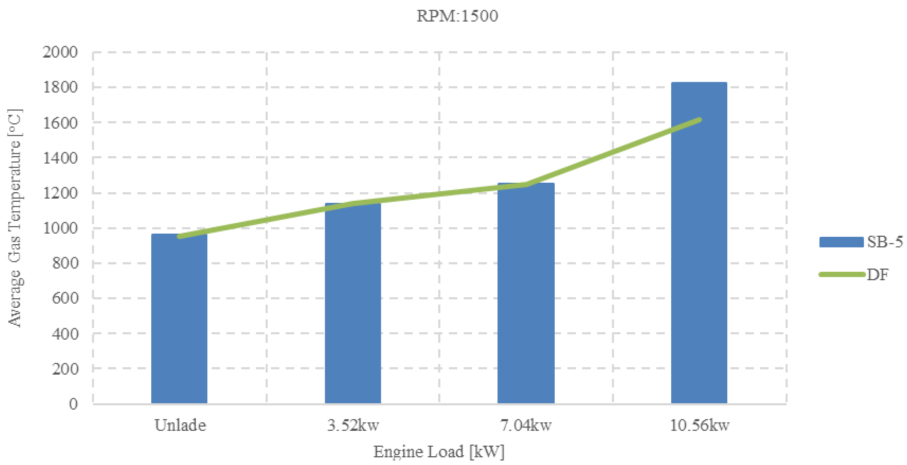


Figure 8. Maximum average gas temperatures depending on engine load.

3.3. Cylinderid gas pressure

The cylinder gas pressure values of the experimental fuels in the case of 7.04 kW load are given in Figure 9, obtained with the test results, and the maximum cylinder pressure values and crank angles of the test fuels at all loads are given in Figure 11. When Figure 9-10, is examined, it is seen that the maximum cylinder gas pressure values of both test fuels (SB-5-DF) occur after the upper dead point. Despite the poor evaporation properties of vegetable oil-based blended fuels, SB-5 fuel produced higher values than DF fuel cylinder pressures due to both its high oxygen content and high hydrocarbon ratio (Türkcan et al., 2009; Yaldiz, 2002)

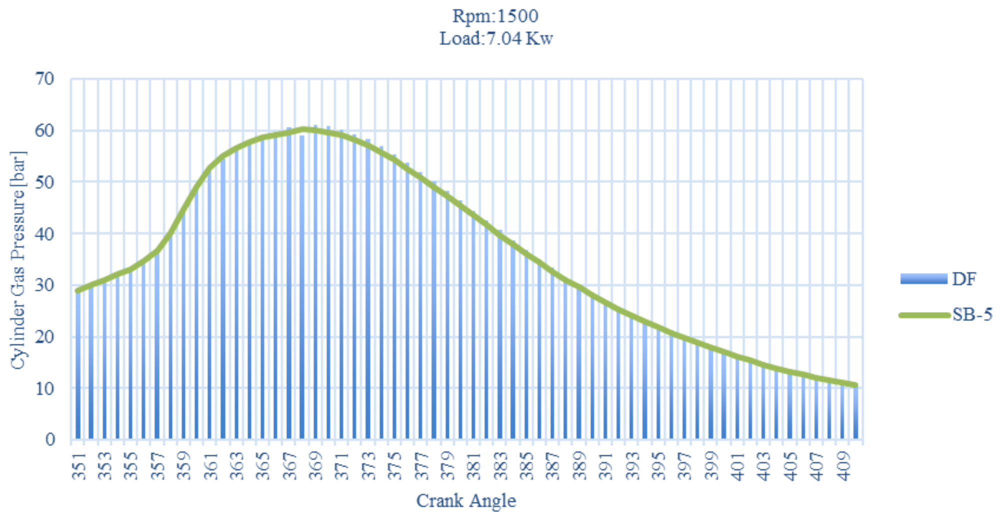


Figure 9. Cylinder pressure variation depending on the crank angle [7.04 kw]

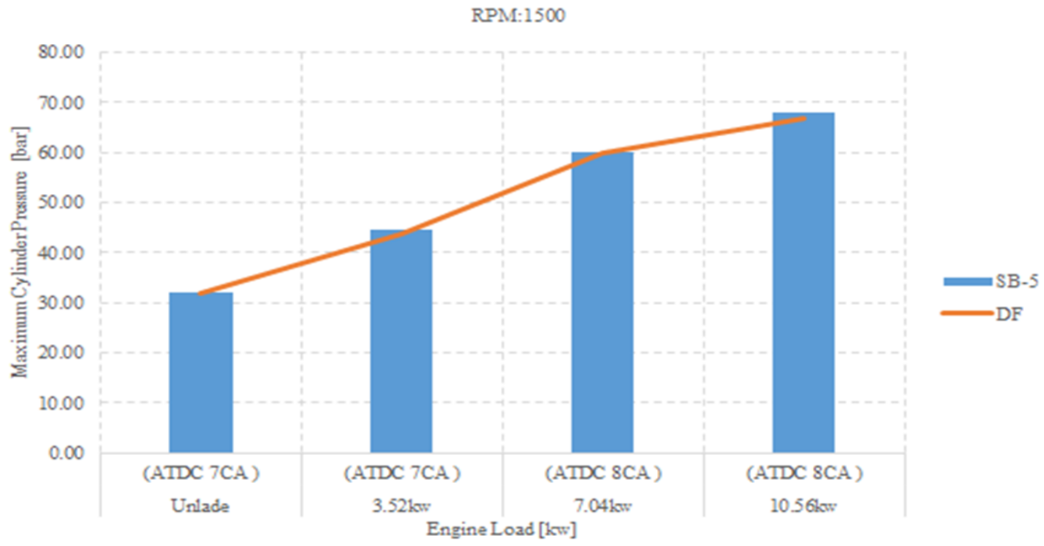


Figure 10. Maximum cylinder gas pressure variations depending on engine load.

3 4. The cumulative heat release

The cumulative heat release maximum values obtained at 1500 fixed engine speeds and with different engine loads are presented in Figure 12, and the cumulative heat release values obtained from the case with 7.04 kW load are presented in Figure 11,.When the obtained results were evaluated, it was determined that the SB-5 blend fuel produced higher temperature values as part of the DF reference fuel. It was thought that these high cumulative values were caused by the high evaporation temperatures of biodiesel fuels and the oxygen contained in it caused an increase in cumulative values by improving combustion.

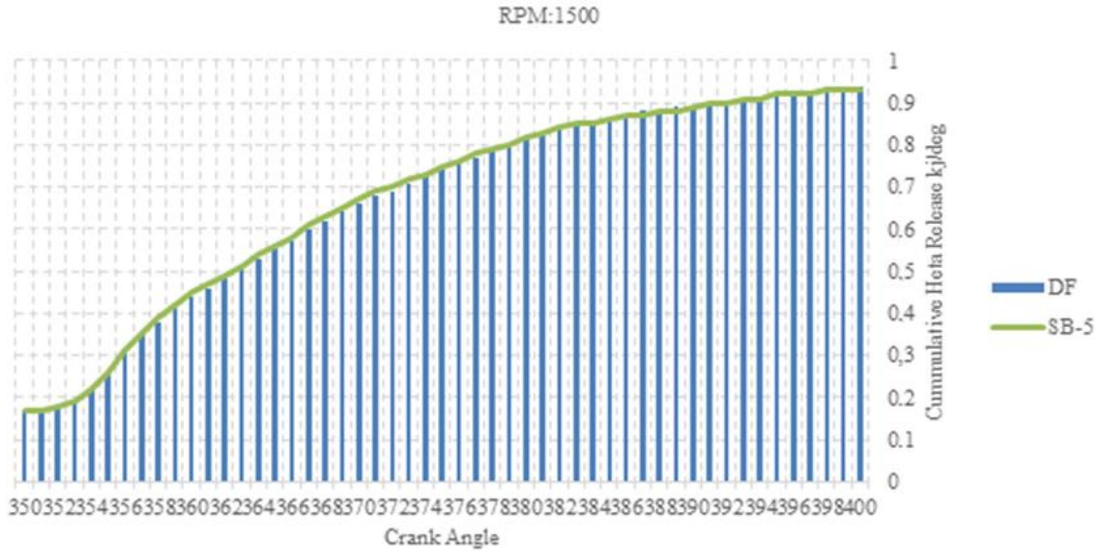


Figure 11. Variations of cumulative heat values depending on the crank angle [7.04 kw]

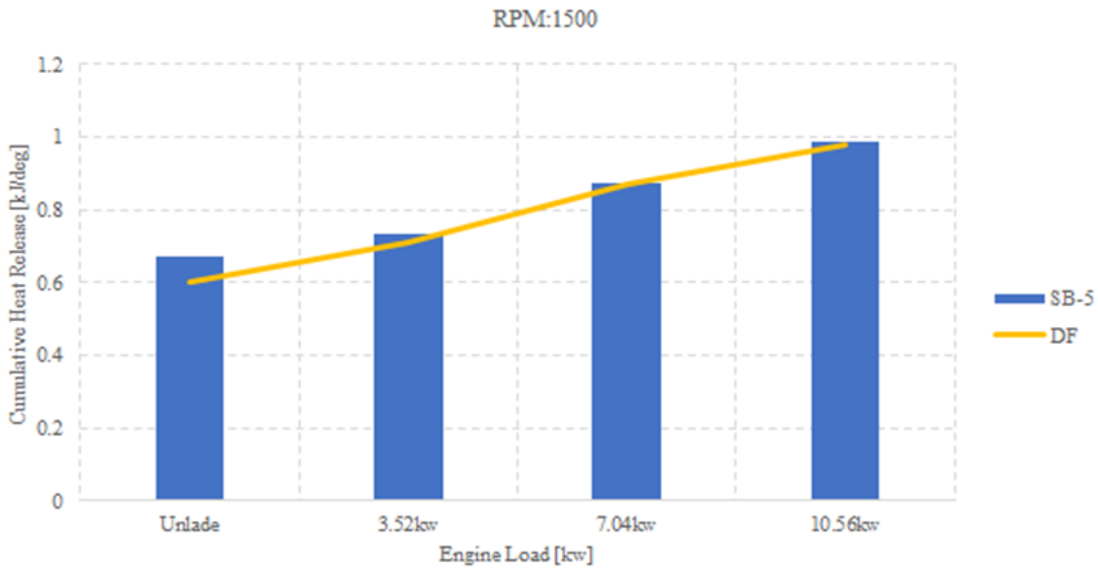


Figure 12. Maximum cumulative heat oscillations due to engine load.

3.5. Knock density

When the figure 13, which is formed by the variations of the knock intensity values in the load condition of 7.04 kW at constant engine speed, depending on the crank angle is examined, It is seen that the knock density values increased a little with the use of SB-5 fuel. The physical and chemical properties of the DF reference fuel are thought to be effective in reducing the ignition delay time. In addition, the high evaporation enthalpy of the Biodiesel blended fuel, the amount of filling taken in, increased the ignition delay time and the impact density value accordingly (Çılğın, 2020).

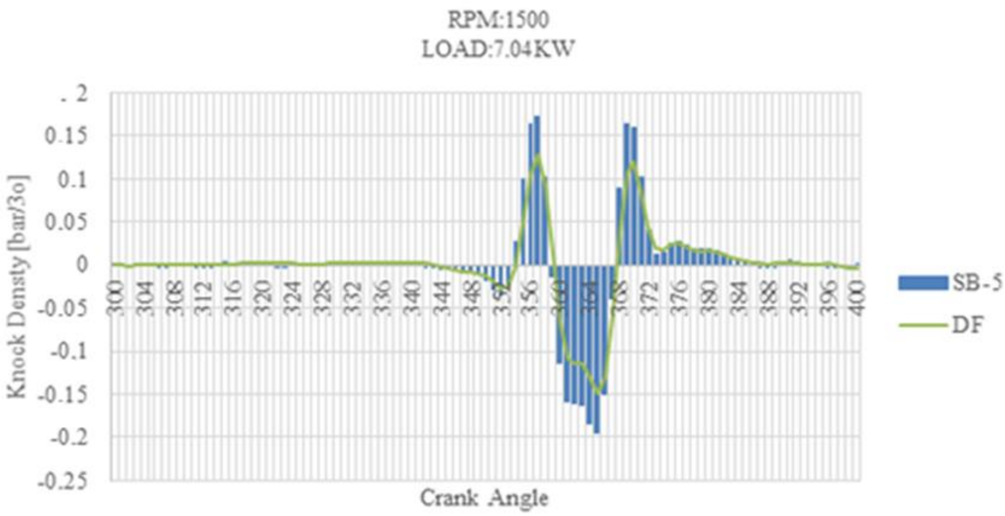
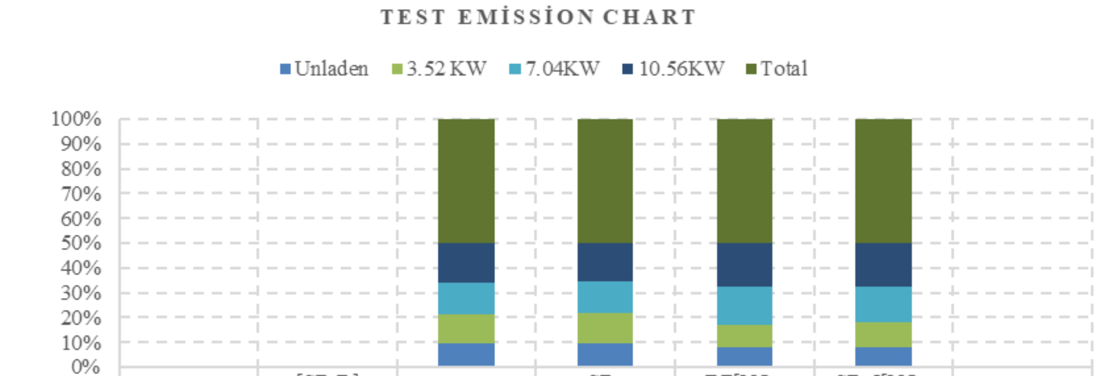


Figure 13. Variation of knock intensity values depending on crank angle [7.04 kw]

3.6. Exhaust gas emission parameters

The main reason for formation is shown in Figure 14, where the CO emission changes with O_2 deficiency in the cylinder are high at low loads. The richness of the mixture at low loads and the insufficiency of turbulence are thought to increase the CO values. As the loading on the engine increases, the high CO emissions have decreased significantly for both fuels. With the use of SB-5 fuel, a reduction of 11.76 % ppm was observed compared to [DF} fuel. The sources of NOx in the atmosphere are vehicle exhaust and fixed combustion plants. These gases enter the natural gas cycle in the atmosphere and complete the chain reactions that result in the formation of nitric acid (HNO_3). The load-dependent variation of nitrogen oxide values measured by the use of test fuels at constant speed is given in şekil 15. With the use of SB-5 fuel, an increase of 4.53 ppm was determined compared to diesel fuel. Hydrocarbons are emission products formed by the removal of incomplete products. This situation can be reduced by improving the combustion efficiency and structural and operational factors that negatively affect combustion. When the HC curves of the test fuels (Figure. 15) SB-5 fuel consumption decreased by 8.00 % ppm compared to the [DF] fuel. Increasing the oxidation of oxygen in essential oils was thought to cause this decrease (Ghazali at all., 2015).



	[DF] [CO%]	[SB-B] [CO%]	DF[HCppm]	SB-5[HCppm]	DF[NOx ppm]	SB-5[NOx ppm]
Total	0	0	135	125	618	646
10.56KW	0	0	43	39	220	225
7.04KW	0	0	34	32	185	189
3.52 KW	0	0	32	30	115	130
Unladen	0	0	26	24	98	102

Figure 14. Exhaust gas emission parameters (CO [%], HC [ppm], NO_X [ppm])

4. Conclusions

The essential oil obtained from the Salvia Candidissima plant has been processed into biodiesel and tested using a reference fuel mixture. Efficient reductions in HC and CO emissions were observed as a result of the experiment when mixed fuel was used, while rises in NO_X emissions were observed. Higher values were obtained from DF fuel using mixed fuel in all combustion data, such as maximum cylinder gas pressure, cumulative heat release, average gas temperatures and knock density values. In view of the combustion and emission values, it can be stated that the essential oil obtained from the Salvia Candidissima plant can be used without modification in diesel engines and that the combustion reaction is significantly improved overall. However, even if the combustion data and emission values of the mixed fuel are improved, the extraction of 6-9 ml of oil from 100 grams of plant biomass prevents it from being economical.

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