OPTIMIZATION OF THERMOPHYSICAL PROPERTIES, COMBUSTION PERFORMANCE AND HARMFUL EXHAUST GASES OF BIODIESEL FUEL WITH NANOPARTICLE ADDITIVES

MEHMET CELIK¹, CIHAN BAYINDIRLI^{2*}

¹ "Karabuk University, Faculty of Engineering, 78050, Karabuk, Türkiye

² "Nigde Omer Halisdemir Universty, Nigde Vocational School of Technical Sciences, 51100, Nigde, Türkiye

Abstract: Increasing use of diesel products causes decrease of oil reserves, global warming, increase in the world average and adverse effects on human health and the environment. Emissions from combustion in engines are directly related to the quality, properties and combustion characteristics of the fuel. Since the physical and chemical properties of the fuel affect the atomization characteristics, it is important for increasing the combustion efficiency. The most important fuel properties affecting the combustion of diesel fuel are cetane number, viscosity, density and calorific value. There are many applications in improving the chemical and physical properties of fuel. One of them is nanoparticle (NPs) additives adding in fuel. In this study, it was aimed to improve fuel properties with optimum additive ratio by adding CeO₂, TiO₂ and Co₃O₄ nanoparticle additives into biodiesel which are produced from cotton and canola oil. The effects of NPs additives in fuel properties such as viscosity, density, lower calorific value and flash points were investigated.

Keywords: environmental pollution, global warming, CeO₂, TiO₂, Co₃O₄, nanoparticles, fuel properties

1. INTRODUCTION

In parallel with population and industrialization, the use of fossil-based fuels has also increased [1]. The diesel engine is widely used to power agriculture, mining and industrial equipment, power generation and public transport. However, diesel engines, as the primary source of environmental pollution; It increases greenhouse gas emissions, global warming and acid rain. Various respiratory and cardiovascular diseases are dangerous consequences of diesel engine emissions, including particulate matter (PM), hydrocarbons (HC), nitrogen oxides (NOx), smoke, carbon monoxide (CO), and various toxic aldehydes and ketones. The need for clean energy sources has arisen from the serious increase in air pollution. In order to reduce the negative effects, emission reduction strategies for diesel engines are constantly changing. Biodiesel is one of the renewable and clean fuels for diesel engines. Biodiesel has the potential to replace fossil fuel and produce less CO, HC and smoke emissions than diesel [2]. Fuel properties of biodiesel such as cetane number, viscosity, density and flash point are higher than diesel fuel. In recent studies, it has been revealed that fuel properties have a significant effect on ignition delay and mixture formation, which are important factors affecting emissions [3]. The quality of combustion in the cylinder is directly related to the physical and chemical properties of the fuel. Properties such as viscosity and density affect combustion [4]. Many methods are used to improve fuel properties. One of the methods widely used

^{*} Corresponding author, email: cbayindirli@ohu.edu.tr © 2022 Alma Mater Publishing House

in recent years is the addition of nanoparticles. Nanoparticle fuel materials exhibit improved active surface area and improve heat transfer between front of flame and unburned fuel particles due to higher metallic thermal conductivities [5]. The addition of nanoparticles to diesel fuel improves the thermophysical properties of the fuel, including catalytic activity, thermal conductivity, surface-to-volume ratio, mass distribution, auto-ignition temperature, cetane number and calorific value [6-8]. However, fuel properties are negatively affected in some nanoparticles. The aim of this study is to determine the effect of nano-sized additives in biodiesel to the thermophysical properties of the fuel. The effects of the improvement in fuel properties on harmful exhaust emissions from engines and the environment were evaluated in paper.

2. MATERIAL AND METHOD

In the study, biodiesel was produced from refined canola oil and refined cottonseed oil by transesterification method. In order to change the fuel properties of biodiesels, 99.5% pure NaOH with 84.01 molecular weight and 99.5% purity methanol with density $0.791\text{-}0.793~kg\cdot L^{-1}$ were used as catalysts during production. Co_3O_4 , CeO_2 and TiO_2 additives were added at the amount of 50 ppm and 75 ppm into the biodiesels. In Table 1, abbreviations and explanations of fuels are given. Table 2 shows the properties of the fuels. The properties of the blended fuels were determined in the accredited fuel analysis laboratory (Figure 1).

Name of fuel		Explanation of fuel			
C0	R0	%100 Methyl Ester (Cotton and Rapeseed)			
CTi50	RTi50	50 ppm TiO ₂ added biodiesel			
CTi75	RTi75	75 ppm TiO ₂ added biodiesel			
CCo50	RCo50	50 ppm Co ₃ O ₄ added biodiesel			
CCo75	RCo75	75 ppm Co ₃ O ₄ added biodiesel			
CCe50	RCe50	50 ppm CeO ₂ added biodiesel			
CCe75	RCe75	75 ppm CeO ₂ added biodiesel			

Table 1. Entitle of blended fuels.



Fig. 1. Mixing of experimental fuels in an ultrasonic mixer.

3. RESULTS AND DISCUSSION

3.1. Viscosity

The chemical composition and viscosity of the fuel are the most important in terms of combustion and atomization [9]. The high viscosity value of biodiesel causes different problems during its use in diesel engines. High viscosity negatively affects fuel performance. Especially at low temperatures, increasing viscosity causes flow problems and low atomization during fuel injection [10]. Figure 2 shows the change in the viscosity of fuels with nanoparticle additives added to biodiesel. CeO₂ and TiO₂ nanoparticle additives decreased the viscosity of the fuel, while Co₃O₄ nanoparticle additive increased the viscosity. Compared to C0 and R0 fuels, the viscosity was decreased by 3.91%-3.65%-10.86% and 4.80% in CTi75-RTi75-CCe75 and RCe75 fuels respectively, at 75ppm additive ratios, while there was an increase of 5.65%-1.53% in CCo75-RCo75 fuels. Considering the effects of fuel properties, lower viscosity facilitates evaporation of the fuel in the cylinder. The sprayed fuel droplet is smaller due to the lower

viscosity and the resulting lower surface tension. Better atomization quality can promote the mixing of fuel and air and provide full combustion environment to reduce emissions [11].

	Table	2. Pro	perties	of tes	t fuels.
--	-------	--------	---------	--------	----------

	Density 15 °C (kg/m³)	Viscosity 40 °C (mm²/s)	Flash Point (°C)	Lower Heating Value (MJ/kg)
C0	886	4.60	175	38.80
CTi50	876	4.48	171	38.92
CTi75	867	4.42	166	39.10
CCo50	895	4.72	179	38.20
CCo75	903	4.86	184	37.72
CCe50	865	4.40	168	38.94
CCe75	849	4.10	157	39.18
R0	892	5.20	179	38.76
RTi50	880	5.07	172	38.90
RTi75	872	5.01	164	39.06
RCo50	899	5.23	186	38.12
RCo75	911	5.28	192	37.86
RCe50	871	5.05	168	38.88
RCe75	862	4.95	159	39.12

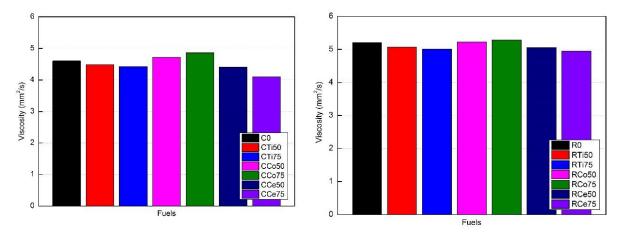


Fig. 2. Viscosity graph of biodiesels with NPs added.

3.2. Density

Density is an important fuel property in terms of engine performance [12]. The characteristic properties of diesel fuel are cetane number, viscosity, aromatic content, etc. properties affect density. For this reason, engine performance data and emission values show changes according to density. High density makes worse fuel atomization and bad homogeneously air-fuel mixture. This situation affects the combustion events as well as the end products of combustion [13]. The density graph of the fuels with additives is shown in Figure 3. CeO₂ and TiO₂ nanoparticle additives decreased the density of the fuel, while Co₃O₄ nanoparticle additive density increased. Compared to C0 and R0 fuels, the density decreased by 2.14% - 2.24% - 4.17% and 3.36% in CTi75- RTi75- CCe75 and RCe75 fuels, respectively. While there was an increase of 1.01% - 0.78% for CCo75 - RCo75 fuels. Depending on the type and size of nanoparticles, mixing with diesel fuel generally causes a small increase in density, although there are studies where the density decreases [14-16]. It is known that the decrease in the viscosity and density of the fuel can cause an increase in BTHE by affecting the fuel atomization and evaporation [17].

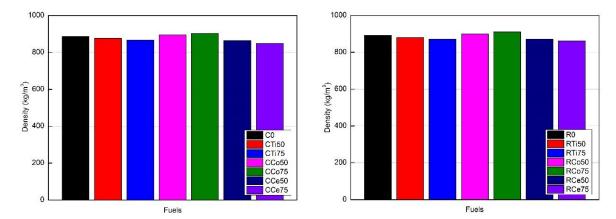


Fig. 3. Density graph of NPs added biodiesel.

3.3. Heating value

The obtained energy from the unit volume or mass of the fuel is called the heating value. Since it represents the amount of energy content of the fuel, it is desired to have a large calorific value [18]. The exhaust gas temperature is affected by the lower heating value of the fuel [19]. While it causes decreases in engine power and torque due to low calorific value, it also causes an increase in fuel consumption [10, 20]. The heating value graph of fuels with additives is shown in Figure 4. Addition of CeO₂ and TiO₂ nano particles to diesel fuel increased to heating value, while Co₃O₄ nano additive decreased to heating value. The heating values of CTi75-RTi75-CCe75 and RCe75 fuels increased by 0.77%-0.77%-0.97% and 0.92%, respectively. But it decreased 2.78%-2.32% in CCo75-RCo75 fuels. High heating value increases the catalyst effect in chemical reactions during the combustion process. The increase in lower calorific values causes an increase in cylinder pressure and heat dissipation [21].

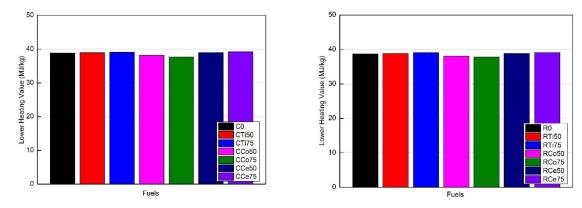


Fig. 4. Heating value graph of NPs added biodiesels.

3.4. Flash point

The lowest temperature at which a fuel can evaporate to form a flammable mixture with air is expressed as the flash point [22]. In other words, it is the lowest temperature at which a combustible mixture occurs at the top of the liquid fuel [23]. The flash point of the fuel is inversely proportional to the volatility. This provides safety in the transportation and storage processes of the fuel but it is seen as a disadvantage in the combustion chamber. The flash point should generally be in the range of 65-150 °C for safety. It should not fall below 36 °C [24]. The flash point of biodiesel fuel is quite good. It does not have a significant effect on the performance change of the engines. The decrease or increase in the flash point does not affect the combustion characteristics. The high flash point of the fuels is suitable for storage and transportation [25]. The flash point graph of fuels with additives is shown in Figure 5. The addition of CeO_2 and TiO_2 nanoparticles into the fuel causes a decrease in the flash point. Adding of Co_3O_4 nano additive increased the flash point.

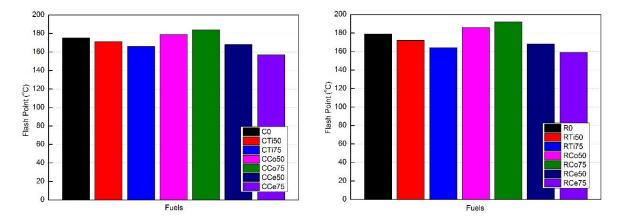


Fig. 5. Flash point graph of NPs added biodiesels.

Improvement of the thermophysical properties of biodiesel such as density, heating value etc. improves combustion performance and combustion end temperatures. This improvement and better atomization reduces HC emissions. Mixing nanoparticles with biodiesel raises the flame temperature, causing more N_2 to oxidize to NOx in the atmospheric air during combustion. Therefore, NOx emissions for nanoparticle blended fuels are higher according to base fuel. One of the reasons for the increase in NOx emissions is the rapid combustion process which effects combustion temperature. Smoke emission forms in the rich fuel zones in the cylinders in course of combustions. The particles of the emission are solid carbon molecules. Thanks to the oxygen provided by additives, reductions in smoke emission can be achieved. Besides that, reduction of viscosity and density provides recovery in fuels, air mixture and reduces the smoke emissions.

4. CONCLUSIONS

In the present study, it was observed that NPs additives added to the fuel affect the fuel properties positively as well as negatively. Considering that the physical and chemical properties of the fuel directly affect the engine performance, combustion and emission characteristics, it is necessary to determine the type of NPs additive added into the fuel well. CeO_2 and TiO_2 nanoparticle additives decreased the viscosity of the fuel, while Co_3O_4 nanoparticle additive increased the viscosity. Compared to C0 and R0 fuels, the viscosity was decreased by 3.91%-3.65%-10.86% and 4.80% in CTi75-RTi75-CCe75 and RCe75 fuels respectively, at 75 ppm additive ratios, while there was an increase of 5.65%-1.53% in CCo75-RCo75 fuels. Addition of CeO_2 and TiO_2 nano particles to diesel fuel improved to density, heating value and flash point, while Co_3O_4 nano additive decreased to them. At the same time, the proportions of the NPs additive to be added to the fuel should be very well optimized.

REFERENCES

- [1] Devarajan, Y., Beemkumar, N., Ganesan, S., Arunkumar, T., An experimental study on the influence of an oxygenated additive in diesel engine fuelled with neat papaya seed biodiesel/diesel blends, Fuel, vol. 268, 2020, p. 117254.
- [2] Murugesan, P., Hoang, A.T., Venkatesan, E.P., Kumar, D.S., Balasubramanian, D., Le, A.T., Pham, V.V., Role of hydrogen in improving performance and emission characteristics of homogeneous charge compression ignition engine fueled with graphite oxide nanoparticle-added microalgae biodiesel/diesel blends, International Journal of Hydrojen Energy, https://doi.org/10.1016/j.ijhydene.2021.08.107, In Press.
- [3] Kobashi, Y., Todokoro, M., Shibata, G., Ogawa, H., Mori, T., Imai, D., EGR gas composition effects on ignition delays in diesel combustion, Fuel, vol. 281, 2020, p. 118730.
- [4] Gürü, M., Karakaya, U., Altınparmak, D., Alıcılar, A., Improvement of diesel fuel properties by using additives, Energy Conversion and Management, vol. 43, no. 8, 2002, p. 1021-1025.
- [5] Ahmed, A., Shah, A.N., Azam, A., Uddin, G.M., Ali, M.S., Hassan, S., Ahmed, H., Aslam, T., Environment-friendly novel fuel additives: investigation of the effects of graphite nanoparticles on performance and regulated gaseous emissions of CI engine, Energy Conversion and Management, vol. 211, 2020, p. 112748.
- [6] Kantamneni, H., Gollakota, A., Nimmagadda, S., Avant-garde Nanotechnology applications in Automotive Industry, Advanced Materials Manufacturing and Characterization, vol.3, no. 107, 2013, p. 195-197.

- [7] Goharshadi, E.K., Samiee, S., Nancarrow, P., Fabrication of cerium oxide nanoparticles: characterization and optical properties, Journal of Colloid and Interface Science, vol. 356, no. 2, 2011, p. 473-480.
- [8] Chen, H.I., Chang, H.Y., Synthesis and characterization of nanocrystalline cerium oxide powders by two-stage non-isothermal precipitation, Solid State Communications, vol. 133, no. 9, 2005, p. 593-598.
- [9] Bednarski, M., Orlinski, P., Wojs, M.K., Sikora, M., Evaluation of methods for determining the combustion ignition delay in a diesel engine powered by liquid biofuel, Journal of the Energy Institute, vol. 92, 2019, p. 1107-1114.
- [10] Azi, H., Investigation on the effect of castor oil biodiesel and diethyl eter usege in a diesel engine on engine performance and emissions, Thesis, Batman Univertsity, 2017.
- [11] Geng, L., Bi, L., Li, Q., Chen, H., Xie, Y., Experimental study on spray characteristics, combustion stability, and emission performance of a CRDI diesel engine operated with biodiesel–ethanol blends, Energy Reports, vol. 7, 2021, p. 904-915.
- [12] Çavgun, E., The experimental investigation of the effects of compression ratio on LPG usage in a dual fuel diesel engine, Thesis, Batman Univertsity, 2019.
- [13] Hanedar, E., Effects of pyrolytic fuel and alcohol additives on combustion and emissions in a diesel engine, Thesis, Düzce University, 2021.
- [14] Chen, A.F., Adzmi, M.A., Adam, A., Othman, M.F., Kamaruzzaman, M.K., Mrwan, A.G., Combustion characteristics, engine performances and emissions of a diesel engine using nanoparticle-diesel fuel blends with aluminium oxide, carbon nanotubes and silicon oxide, Energy Conversion and Management, vol. 171, 2018, p. 461-477.
- [15] D'Silva, R., Binu, K.G., Bhat, T., Performance and emission characteristics of a C.I. engine fuelled with diesel and TiO_2 nanoparticles as fuel additive, Materials Today: Proceedings, vol. 2, no. 4-5, 2015, p. 3728-3735.
- [16] Patil, D.S., Chopade, D.A., Kumbhalkar, M.A., Experimental investigation of effect of cerium oxide nanoparticles as a fuel additives in cottonseed biodiesel blends, MAYFEB Journal of Mechanical Engineering, vol. 1, 2018, p. 1-12.
- [17] Das, A.K., Hansdah, D., Panda, A.K., Thermal balancing and exergetic performance evaluation of a compression ignition engine fuelled with waste plastic pyrolytic oil and different fuel additives, Energy, vol. 229, 2021, p. 120629.
- [18] Tillem, İ., Production and use of biodiesel as an alternative fuel for diesel engines, Thesis, Pamukkale University, 2005.
- [19] Pulkrabek, W.W., Engineering fundementals of the internal combustion engine, Prentice Hall Upper Saddle River, New Jersey, 2004, p. 50-289.
- [20] Duran, G., The investigation of the usability of ethanol additive microalgae oil in a diesel engine, Thesis, Fırat University, 2017.
- [21] Sathyamurthy, R., Balaji, D., Gorjian, S., Muthiya, S.J., Bharathwaaj, R., Vasanthaseelan, S., Essa, F.A., Performance, combustion and emission characteristics of a DI-CI diesel engine fueled with corn oil methyl ester biodiesel blends, Sustainable Energy Technologies and Assessments, vol. 43, 2021, p. 100981.
- [22] Eskici, B., Investigation of the effects of the use of biodiesel fuel on a combustion process and engine tribology in a diesel engine, Thesis, Sivas Cumhuriyet University, 2019.
- [23] Arslan, A.B., Investigation of the effect of CeO₂ nanoparticle addition in diesel fuel on engine performance and emissions, Thesis, Karabuk University, 2022.
- [24] Aydın, B., Investigation of the effect of biodiesel added with nano fuel additives on diesel engine performance and emissions, Thesis, Karabuk University, 2022.
- [25] Yaşar, M.F., One-dimensional modeling of performance and emission characteristics of a methane additive diesel engine, Thesis, Sakarya Uygulamalı Bilimler University, 2020.