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INVESTIGATION OF THE EFFECT OF NANOPARTICLE ADDITIVES ON THE REFRACTIVE INDEX AND DENSITY OF GASOLINE

NANOPARTİKÜL İLAVESİNİN BENZİNİN KIRILMA İNDİSİ VE YOĞUNLUĞU ÜZERİNDEKİ ETKİSİNİN ARAŞTIRILMASI

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ABSTRACT

In this study, the use of Al_2O_3 and TiO_2 nano particles with a size of 12 nm and a purity of 99.9% as gasoline fuel additives was investigated. Fuel mixtures were prepared using a 3-level factorial design technique, and density and refractive index values were determined. Al_2O_3 nano particles, due to their high surface area, increased the density by 0.17% (3.5 ppm) and 1.22% (7 ppm), while TiO_2 nano particles increased the density by 0.22% (3.5 ppm) and 1.26% (7 ppm). It was observed that the nano particle with a higher surface area had a less significant effect on density. The refractive index values decreased by 0.11% (3.5 ppm) and 0.14% (7 ppm) for Al_2O_3 nano particles, and by 0.21% (3.5 ppm) and 0.24% (7 ppm) for TiO_2 nano particles. This study highlighted the importance of particle size, purity, and surface area in the selection of nano particles. Based on the evaluations and preliminary tests, nano particle levels above 15 ppm exhibited a tendency for agglomeration in the fuel. It is crucial to limit the total concentration to 15 ppm, especially for nano particles with a high surface area like Al_2O_3, to achieve homogeneous fuel.

Keywords: Aluminum oxide, titanium dioxide, gasoline additive, refractive ındex, density

ÖZET

Bu çalışmada, 12 nm boyutunda ve %99.9 saflıktaki Al_2O_3 ve TiO_2 nano partiküllerinin benzin yakıt katkı maddesi olarak kullanımı incelenmiştir. Partikül ilave edilen yakıt karışımlarının yoğunluk ve kırılma indisi değerleri benzin yakıtıyla karşılaştırılmıştır. 3 seviyeli faktöriyel tasarım tekniği kullanılarak yakıt karışımları elde edilmiş, yoğunluk ve kırılma indisi değerleri belirlenmiştir. Sonuçlar, Al_2O_3 nano partikülünün yüksek yüzey alanı nedeniyle yoğunluğu %0,17 (3.5 ppm) ve %1,22 (7 ppm) oranında artırdığını göstermiştir. TiO_2 nano partikülünün ise yoğunluğu %0,22 (3.5 ppm) ve %1,26 (7 ppm) oranında artırdığı belirlenmiştir. Yüzey alanı yüksek olan nano partikülün yoğunluk üzerinde daha az etkili olduğu görülmüştür. Kırılma indisi değerleri ise Al_2O_3 nano partikülünde %0,11 (3.5 ppm) ve %0,14 (7 ppm) azalırken, TiO_2 nano partikülünde ise %0,21 (3.5 ppm) ve %0,24 (7 ppm) azaldığı tespit edilmiştir. Bu çalışma, nano partikül seçiminde boyut, saflık ve yüzey alanının önemli olduğunu ortaya koymuştur. Yapılan değerlendirmeler ve ön testler neticesinde, 15 ppm üzerindeki nano partikül seviyelerinin yakıt içerisinde topaklanma eğilimi göstermektedir. Özellikle yüksek yüzey alanına sahip Al_2O_3 gibi nano partiküller için toplam oranın 15 ppm'yi

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aşmaması homojen bir yakıt elde edilmesi için önemli bir parametredir.

Anahtar Kelimeler: Alüminyuma oksit, titanyum dioksit, benzin katkı maddesi, kırılma indisi, yoğunluk

INTRODUCTION

Globally, the demand for energy is continuously increasing due to the growing world population. Among various energy sources, gasoline fuel derived from the refining of crude oil plays a crucial role as a primary energy source in numerous industrial applications, including automobiles, aircraft, and agricultural machinery. As the world population expands, so does the number of vehicles on the roads. The transportation sector heavily relies on gasoline fuel to meet its energy needs. Automobiles, being the most common mode of transportation, heavily depend on gasoline for their operations. Similarly, aircraft and agricultural machinery also heavily rely on gasoline as their primary fuel source.(Acaroğlu et al., 2018). This situation brings along with it the problems of environmental pollution caused by exhaust emissions, depletion of oil reserves, and disruption of supply-demand balance. The characteristics that fuels should meet are determined by international standards, and gasoline engine manufacturers produce engines that comply with these standards. However, these standards prioritize acceptable engine performance and emission values, focusing on cost-effective production. (Reif, 2015). The reason why different countries worldwide develop their gasoline formulations in their domestic refineries, particularly considering the climatic and geographical conditions of developed countries, is because international standards allow flexibility in gasoline composition. In Europe, for example, there are various gasoline options such as 95, 98, and 100 octane, while in the United States, fuels with higher oxygen content that provide better performance in winter conditions are commercially available. These variations in gasoline formulations allow countries to cater to their specific regional needs and optimize performance under different environmental conditions.

Gasoline additives used in fuel can be categorized based on their properties as anti-knock agents, stabilizers, corrosion inhibitors, combustion enhancers, and detergent additives. (Srivastava & Hancsók, 2014). Although commonly used gasoline additives include chemicals such as aromatics, phenols, phosphorus, and lead tetraethyl, nano particles can also be used as additives in fuel (Kotia et al., 2020). Nano particles with sizes ranging from 1 to 100 nm exhibit extraordinary properties due to their small size and often behave differently from larger structures. As the size decreases, the chemical activation and surface area of the particles increase. Increased chemical activation enhances the particles' ability to interact with the surrounding environment, while increased surface area increases the number of particles per unit volume. Smaller-sized materials also have a reduced number of chemical bonds per unit area. Consequently, as particle size decreases, their melting points significantly decrease. For example, the melting temperature of gold in bulk structures is 1337 K, whereas for particles with a size of 6 nm, it decreases by approximately 200 K. (Naito et al., 2018). One of the most important factors contributing to the increased chemical activation of materials as their size decreases is the increase in surface area. The increased surface area enhances the material's propensity for reactions and chemical behavior, making nano-sized materials much more reactive compared to bulk materials. Therefore, the addition of a small amount of nanoparticle can effectively enhance the properties of fuels (Khan et al., 2022; Dehhaghi et al., 2021; Hatami et al., 2020; Karmakar, 2012).

Density is one of the properties that gasoline fuel needs to meet, which measures the amount of substance within a given volume. Density is directly proportional to the amount of substance in a given volume. Refractive index, on the other hand, is a parameter that measures the amount of reflection or transmission of electromagnetic waves by a fuel (Gahlyan et al., 2020). This parameter is related to the dielectric function of the fuel, and the value of the dielectric function is dependent on the density of the fuel's electric polarization. This means that the reflection or transmission of electromagnetic waves by fuels is dependent on their densities. Generally, denser fuels have lower refractive indices because dense materials have more intense electric polarizations, resulting in less reflection or transmission of waves (Nita et al., 2016; Nikolaev et al., 2015). Similarly, less dense fuels have higher refractive indices because the electric polarizations of less dense materials are less intense, resulting in more reflection or transmission of waves.

There is insufficient research available in the literature regarding the density and refractive index of nano-particles added to gasoline fuel. Density, which is an important property providing information about fuel classification, calorific value, and knock resistance, along with the refractive index value that provides information about hydrocarbon content, were determined through measurements using fuel blends obtained by adding Al_2O_3 and TiO_2

nano-particles in different proportions to gasoline fuel. The aim of this study was to elucidate the effects of nano-particle additives on the density and refractive index values of gasoline.

MATERİAL AND METHOD

Fuel blends were prepared using 12 nm-sized Al_2O_3 particles and TiO_2 particles with a purity of 99.9%. Pre-screening tests were conducted to determine the fuel ratios, and the total particle concentration was limited to a maximum of 14 ppm due to observed agglomeration when exceeding 15 ppm. Ultrasonic homogenizer and mechanical mixer were used during the preparation of the blends to ensure the uniform dispersion of particles in the fuel. As shown in Table 1, a factorial design method with 3 levels was used for each nano-particle, resulting in 8 mixtures containing particles. Shell's FuelSave unleaded gasoline was used as the base fuel for comparison. The fuel and particle specifications used in the tests are provided in Table 2.

Table 1: Nano Particle Blending Ratios

Factors	*Levels*		
Al_2O_3 (ppm)	*0*	*3.5*	*7*
TiO_2 (ppm)	*0*	*3.5*	*7*

Table 2: Fuel Specifications

Feature	Gasoline	Aluminium Oxide	Titanium Dioxide
Molecular Formula	C_XH_Y	Al_2O_3	TiO_2
Molecular Weight (g/mol)	-	101.96	79.86
Density (g/cm^3)	0,740	3.94	4.23
Flashing Point (°C)	<-40	-	-
Auto Ignition Point (°C)	>250	-	-
Octane Number	95	-	-
Thermal Conductivity (W/mK)	120	30	11.8
Boiling Point (°C)	47	2977	2972
Lov Heat Value (kJ/kg)	43430	-	-

The density measurements of the 8 different fuel blends containing nano particles were conducted at 20°C using a Mettler Toledo DensitoPro device and compared to standard gasoline, as provided in Table 3. Additionally, the refractive index values of the fuel blends were measured using a Rudolph Research J357 refractometer with the specifications given in Table 4. All measurements were performed with 5 repetitions, and the averages were calculated.

Table 3: Density Measurement Device Specifications

Feature	Attribute
Model	MT DensitoPro
Measurement Range	0 - 3 g/cm^3
Sensitivity	±0,001 g/cm^3
Repeatability	±0,0005 g/cm^3
Resolution	0,0001 g/cm^3
Sample Temp Range	0 - 50 °C

Table 4: J357 Refractometer Specifications

Feature	Attribute
Model	RR J357 Refraktometre
Measurement Range	1.26 - 1.72
Resolution	0.00001
Repeatability	±0.00002
Sensitivity	±0.00002
Optical Wave Length	589.3 nm
Prism Structure	Synthetic Sapphire
Temp Control Range	10º C - 100º C
Temp Control Sensitivity	±0.05º C
Ambiennt Temp Limit	5ºC - 40º C

Research Findings

According to the measurements, for both nano particles, it was observed that the density value of the fuel without Al_2O_3nano particles (gasoline) was 0.7402 g/cm3, while it increased to 0.7415 g/cm3 with a nano particle concentration of 3.5 ppm, as shown in Figure 1. This indicates an increase in density by 0.17%. When the nano particle concentration was increased to 7 ppm, the density value reached 0.7493 g/cm3, corresponding to a 1.22% increase. Regarding the refractive index values, it was found that the highest value was 1.42302 for the gasoline fuel. In the fuel blend with 3.5 ppm Al_2O_3 nano particles (Fuel 2), this value decreased by 0.11% to 1.42134. In the fuel blend with 7 ppm Al_2O_3 (Fuel 3), there was a 0.14% decrease, and the refractive index level was measured as 1.42096.

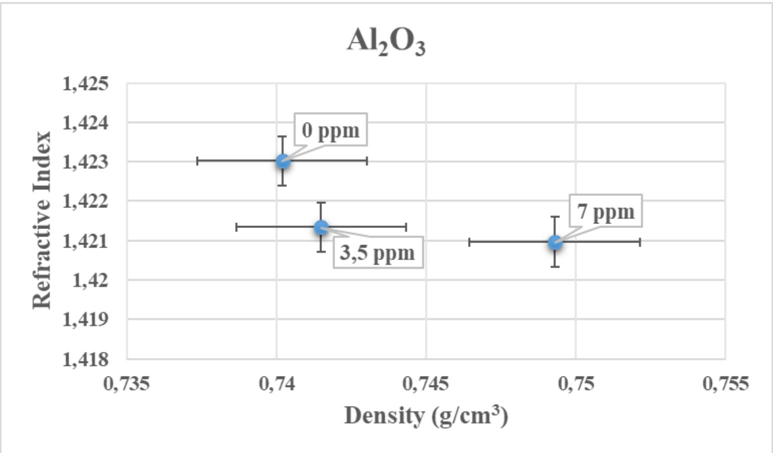

Figure 1: The Effect of Al_2O_3 Nano Particles on Refractive İndex and Density

According to Figure 2, the effect of TiO_2 nano particles on the refractive index and density values is presented. The fuel with 3.5 ppm TiO_2 nano particles showed an increase in density by 0.22% compared to gasoline fuel, with a measured value of 0.7419 g/cm3. In the fuel with 7 ppm TiO_2, the density value further increased by 1.26% to reach 0.7496 g/cm3. The refractive index value decreased by 0.21% in the fuel with 3.5 ppm TiO_2 nano particles, measuring 1.41997, and decreased by 0.24% in the fuel with 7 ppm TiO_2 nano particles, measuring 1.41959. Considering the current situation, the changes in density and refractive index caused by both nano particle additives are within the acceptable range and in compliance with ASTM standards.

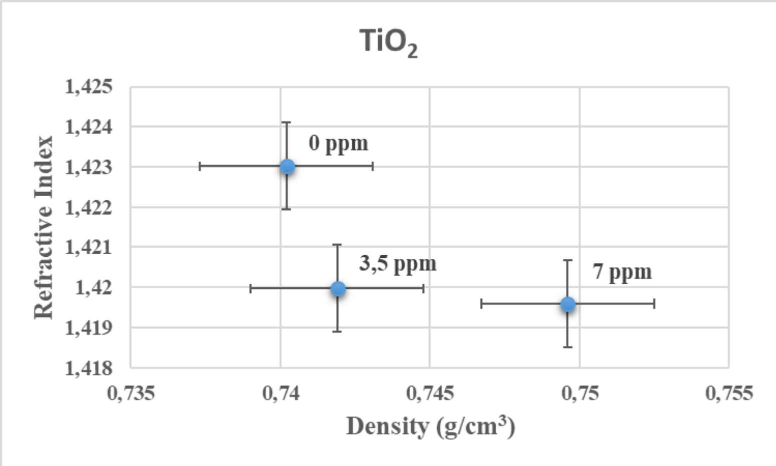

Figure 2: The Effect of TiO_2 Nano Particles on Refractive İndex and Density

All measurements conducted for the mixture quantities obtained through the 3-level factorial design technique are presented in Table 5. Prediction functions were derived from the data obtained in the table using the 3-level factorial design technique. These equations enable the prediction of density and refractive index values. The 1st equation, derived as a function of nano particle quantities, allows for the prediction of density values, while the 2nd equation enables the prediction of refractive index values with an accuracy of over 90%.

Table 5: Measurement Results of All Blends

Fuel	Al_2O_3 (ppm)	TiO_2 (ppm)	Density (g/cm^3)	Ref. Index
Gasoline	0	0	0.7402	1.42302
Fuel 1	3.5	0	0.7415	1.42134
Fuel 2	7	0	0.7493	1.42096
Fuel 3	0	3.5	0.7419	1.41997
Fuel 4	3.5	3.5	0.7444	1.41989
Fuel 5	7	3.5	0.7468	1.41982
Fuel 6	0	7	0.7496	1.41959
Fuel 7	3.5	7	0.7501	1.41929
Fuel 8	7	7	0.7518	1.41813

$$Density = 0,74211 + 0,00216327 * Al_2O_3 + 0,000196599 * TiO_2 - 0,000132945 * {Al_2O_3}^2 - 0,000142274 * Al_2O_3 * TiO_2 + 0,0000833819 * TiO2^2 \quad (1)$$

$$Refraktive\ Index = 1,42256 - 0,000260476 * Al_2O_3 - 0,000721429 * TiO_2 + 0,00000612245 * {Al_2O_3}^2 + 0,0000122449 * Al_2O_3 * TiO_2 + 0,0000404082 * {TiO_2}^2 \quad (2)$$

RESULTS

In this study, fuel mixtures were prepared by mixing Al_2O_3 and TiO_2 nano particles with particle sizes of 12 nm and purity of 99.9%, and surface areas of 378.80 m2/g and 48.8 m2/g, respectively, with gasoline at concentrations of 0, 3.5, and 7 ppm. The refractive index and density values of the fuel mixtures were compared with those of gasoline. The quantities of the fuel mixtures were determined using the 3-level factorial design technique, and prediction functions were obtained. The comparison revealed that the Al_2O_3 nano particle with higher surface area increased the density by 0.17% at the 3.5 ppm level and by 1.22% at the 7 ppm level. On the other hand, the TiO_2 nano particle with lower surface area increased the density by 0.22% at the 3.5 ppm level and by 1.26% at the 7 ppm level. Despite having the same particle size and purity ratios, the different surface areas of the nano particles caused variations in their densities, with the higher surface area particle having a lower impact on density. The refractive index values decreased by 0.11% and 0.14% at the 3.5 ppm and 7 ppm levels, respectively, for the Al_2O_3 nano particle. Similarly, for the TiO_2 nano particle, there was a decrease of 0.21% and 0.24% at the 3.5 ppm and 7 ppm levels, respectively. These results fall within the acceptable range according to ASTM standards. This study highlighted the importance of particle size, purity, and surface area in the selection of particles added to gasoline. Preliminary screening tests revealed a tendency for particle aggregation in gasoline at levels above 15 ppm. Particularly, ensuring that the total ratio of high-surface-area nano particles does not exceed 15 ppm can prevent aggregation. The study demonstrated that the use of Al_2O_3 and TiO_2 nano particles can affect fuel properties in internal combustion engines, emphasizing the need for further research. The findings will contribute to a better understanding of how the addition of nano particles to gasoline can affect engine performance and emissions.

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