



Improvement of Stability and Thermal Conductivities of Oil-Based Nanofluids in Optimum Acid-Base Admixture Values

Yağ Bazlı Nanoakışkanların Optimum Asit-Baz Katılım Değerlerinde Kararlılık ve Isıl İletkenliklerinin İyileştirilmesi

Fevzi ŞAHİN¹, Lütfü NAMLI²

¹Ondokuz Mayıs Üniversitesi, Mühendislik Fakültesi, Makine Mühendisliği Bölümü, Samsun
• fevzi.sahin@omu.edu.tr • ORCID > 0000-0002-4808-4915

²Ondokuz Mayıs Üniversitesi, Mühendislik Fakültesi, Makine Mühendisliği Bölümü, Samsun
• lnamli@omu.edu.tr • ORCID > 0000-0001-9758-0889

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Sorumlu Yazar / Corresponding Author: Fevzi ŞAHİN

IMPROVEMENT OF STABILITY AND THERMAL CONDUCTIVITIES OF OIL-BASED NANOFLUIDS IN OPTIMUM ACID-BASE ADMIXTURE VALUES

ABSTRACT

In this work, it has been aimed to improve the stability and thermal conductivity of the nanofluids that use the heat transfer oil, which is frequently used in the industry, as the base fluid. For this purpose, the nanofluids were synthesized by using Al_2O_3 (alumina) and TiO_2 (titanium dioxide) nanoparticles in the mass ratios of 1%, 2% and 3% and the heat transfer oil as the base fluid. H_2SO_4 (sulphuric acid) or KOH (potassium hydroxide) at 5 N (normality) valence solutions were added separately to the prepared nanofluids at the determined volumetric ratios ($10^{-3}\%$, $3.5 \times 10^{-3}\%$, $5.3 \times 10^{-3}\%$ and $8 \times 10^{-3}\%$). By being prepared nanofluids separately with acid and base, the highest enhancement rates in the stability appeared were about 24% for 2% Al_2O_3 by mass and $3.5 \times 10^{-3}\%$ H_2SO_4 by volume mixture in the alumina-acid case and about 50% for 1% Al_2O_3 by mass and $5.3 \times 10^{-3}\%$ KOH by volume mixture in the alumina-base case. Similarly, the highest enhancement rates in the stability of the nanofluids were about 75% for 3% TiO_2 by mass and $10^{-3}\%$ H_2SO_4 by volume mixture in the titanium dioxide-acid case and about 77% for 2% TiO_2 by mass and $10^{-3}\%$ KOH by volume mixture in the titanium dioxide-base case.

Keywords: Nanofluid, Heat Conduction Coefficient, Stability, Al_2O_3 Nanoparticle, TiO_2 Nanoparticle.

Highlights

- Stability study with acid-base addition for oil-based nanofluids.
- Comparison of nanofluid heat conduction coefficient with mathematical and experimental models
- A new method for the stability of oil-based nanofluids.



YAĞ BAZLI NANOAKIŞKANLARIN OPTİMUM ASİT-BAZ KATILIM DEĞERLERİNDE KARARLILIK VE ISIL İLETKENLİKLERİNİN İYİLEŞTİRİLMESİ

ÖZ

Bu çalışmada, endüstride sıklıkla kullanılan ısı transfer yağını baz akışkan olarak kullanan nanoakışkanların kararlılığının ve ısı iletkenliğinin artırılması amaçlanmıştır. Bu amaçla, %1, %2 ve %3 kütle oranlarında Al_2O_3 (alümina) ve TiO_2 (titanyum dioksit) nanopartikülleri ve baz akışkan olarak ısı transfer yağı kullanılarak nanoakışkanlar sentezlenmiştir. Hazırlanan nanoakışkanlara belirlenen hacimsel oranlarda (10^{-3} , $3,5 \times 10^{-3}$, $5,3 \times 10^{-3}$ ve 8×10^{-3}) H_2SO_4 (sülfürik asit) veya KOH (potasyum hidroksit) 5 N (normalite) değerlikli çözeltileri ayrı ayrı eklenmiştir. Nanoakışkanlar asit ve baz ile ayrı ayrı hazırlanarak, ortaya çıkan stabilitedeki en yüksek artış oranları, alümina-asit durumunda kütlece %2 Al_2O_3 ve hacimce $3,5 \times 10^{-3}$ H_2SO_4 karışımı için yaklaşık %24 ve alümina-baz durumunda kütlece %1 Al_2O_3 ve hacimce $5,3 \times 10^{-3}$ KOH karışımı için yaklaşık %50 olmuştur. Benzer şekilde, nanoakışkanların stabilitesindeki en yüksek artış oranları, titanyum dioksit-asit durumunda kütlece %3 TiO_2 ve hacimce 10^{-3} H_2SO_4 karışımı için yaklaşık %75 ve kütlece %2 TiO_2 ve 10^{-3} için yaklaşık %77 olmuştur.

Anahtar kelimeler: Nanoakışkan, Isı İletim Katsayısı, Stabilité, Al_2O_3 Nanopartikül, TiO_2 Nanopartikül.



1. INTRODUCTION

Considering the rapidly running out of conventional energy resources, the importance of efficiency in energy use is increasing with each passing day. In energy systems, one of the most important subjects in which efficiency is investigated is the heat transfer systems. Heat transfer fluids such as water and oil are used in heat transfer systems. The thermal properties of these fluids are crucial for the energy efficiency of the system to be used. There are many studies on the heat transfer fluids used in heat transfer processes with the technological developments [1]–[6]. On the other hand, numerous scientific advances have been taken place in the field of heat transfer and energy with nanofluids. One of the most important restrictions on the practical use of the findings obtained from studies is the stability of the nanofluid. These studies attracting attention in recent years are about the synthesizing new nanofluids which are developed thermal properties, adding the materials which can be produced in nanoscale to heat transfer fluids called base fluid at a certain volume and mass fractions. These new fluids are called in the literature as

nanofluids. Oxides in nanoscale dimension used in obtaining nanofluids are Al_2O_3 (alumina), CuO (copper oxide) and TiO₂ (titanium dioxide). Metals are Fe (iron) and Cu (copper). Another material used in synthesizing nanofluids is graphene. Numerous studies of nanofluids prepared by adding nanoparticles with heat transfer fluid have shown that these new fluids bring thermally a successful conclusion [7]–[9]. The increase in the thermal conductivity of the nanofluid has been shown to arrive at the conclusion better than the increase from the solid-liquid mixture made in the micro dimensions that are being applied more prior [10].

Nanofluids are not simple solid-liquid mixtures [11]. They are prepared by a certain method and techniques. Nanofluids commonly have two basic production methods. These are one-step method and two-step method in the literature [8]. In the one-step method, the nanoparticles desired to be added into the base fluid are produced in the fluid. In the two-step method, previously produced nanoparticles are added directly into the base fluid. In both methods, it is expected that the nanoparticles will be homogeneously dispersed in the base fluid and that the nanoparticles will not agglomerate to form precipitates. The large surface area and high surface energy of the nanoparticles cause agglomeration and sedimentation in the nanofluids [12], [13]. Appropriate dispersion methods should be applied to prevent the formation of sediment and to ensure long-term stability. The most common methods in the two-step method are ultrasonic dispersing and deagglomeration, surfactant addition, and determination of the optimal pH ratio for aqueous mixtures [11], [13].

The stability of the nanofluid depends on the characteristics of the nanoparticle and the base fluid [14]. Agglomeration caused by deteriorating stability affect heat transfer in the negative direction [15]. In nanofluids studies, long-term stabilization by the suspension of nanoparticles is one of the most important issues. In nanofluids where stability is not provided, it is unlikely that the heat transfer properties will improve relative to the basic flow and contribute to their widespread use. The gravitational force acting on the desired nanoparticles suspended in the base fluid is negligible [16]. Nanoparticles dispersed in the base fluid tend to agglomerate by interacting with each other [17]. With increasing agglomeration, the gravitational force becomes more effective and the collapse starts to occur. A theory has been developed by DeJaguin, Verwey, Landau and Overbeek (DLVO) for the stability of particles in the fluid [18]. This theory describes the forces acting on the nanoparticles in the nanofluid depending on the Van der Waals forces and the electrostatic forces of the surfaces. The Van Der Waals forces are attracting molecules of the same species. For this reason, Van der Waals forces cause the nanoparticles dispersed in the base fluid to agglomerate by time [15]. Electrostatic forces are the pushing force of the same kind of charged particles to each other and the pulling force of charged particles of different kinds to each other, which is a phenomenon that occurs between charged particles. To ensure stability in the nanofluids, it is

expected that the repulsive forces that balance the tensile forces between the particles will dominate [8]. The stability of the nanofluids is strongly dependent on the surface loads of the particles. The presence of high surface charges on the surfaces of the nanoparticles in the nanofluids is necessary to achieve good stability [19].

The scale of the surface charge is expressed by the zeta potential. Zeta potential, a measure of the surface charge, is provided in the nanofluid studies of stability provided in the range of ± 40 -60 mV, and excellent stability at higher values than 60 mV is obtained [8]. There are many studies in the literature where zeta potential is measured to determine stability in nanofluids [15], [20]–[24]. In the majority of the studies performed, the zeta potential value for stability was obtained by determining the pH values of the nanofluid at optimum ratios. The pH value can be easily controlled by acid and base solutions prepared at certain ratios when the basic fluid is water. But, it is not possible to mention the pH concept in oil-based solutions. Instead, the method of directly interfering with the surface charges of nanoparticles with acid and base solutions is a useful and applicable method.

The aim of this work is to improve the stability and thermal conductivity of heat transfer oil used industrially in the field of rarely worked oil-based nanofluids in the field of nanofluids. In order to investigate this deficiency in oil-based nanofluids, the acid (H_2SO_4) and base (KOH) solutions are mixed directly with the nanoparticle at the volume ratio determined in very small quantities, and then the oil-based nanofluids are prepared by ultrasonic dispersing. Suitable acid or base ratios have been determined for stability in nanofluids prepared separately with the heat transfer oil at 1%, 2% and 3% by mass of TiO_2 (titanium dioxide) and Al_2O_3 (alumina) nanoparticles. The effects of the prepared H_2SO_4 (sulphuric acid) and KOH (potassium hydroxide) at 5 N (normality) valence and base solutions on the stability of the nanofluids at the determined volumetric ratios ($10^{-3}\%$, $3.5 \times 10^{-3}\%$, $5.3 \times 10^{-3}\%$ and $8 \times 10^{-3}\%$) were measured by the sedimentation method. The nanofluids prepared at different acid and base ratios were compared with those without additives. As a result of the work performed, the thermal improvements in the nanofluids synthesized are determined. In addition, the stability of the nanofluids, whose basic fluid is oil, was ensured by acid-base additives, which is not common in the literature, and measured by sedimentation method.

2. EXPERIMENTAL STUDIES

2.1. Preparation of Nanofluids

In this study, the two-step method of nanofluid synthesis was used. The nanoparticles were slowly added by mechanical mixing method into the oil-based fluid mixed with acid or base solutions in defined proportions. It is then dispersed in the

base fluid for the periods specified by the ultrasonic liquid processor. The preparation diagram of the nanofluids is given in Figure 1. Nanoparticles are commercially bought from Nanostructured & Amorphous Materials (NanoAmor), Inc. USA. As the nanoparticles, alumina (Al_2O_3) in the size of 20-30 nm and TiO_2 (titanium dioxide) in the size of 30-40 nm were used. Heat transfer oil is used as the base fluid in the preparation of the nanofluid. The nanoparticles were weighed with a precision scale of 0.1 mg. An ultrasonic liquid processor with a power of 750 W was used to disperse the nanoparticles in the base fluid. Nanoparticles containing Al_2O_3 nanoparticles in ratios of 1%, 2% and 3% by mass were synthesized by an ultrasonic liquid processor applied for an average of an hour. The TiO_2 nanoparticles were synthesized with mass ratios of 1%, 2% and 3% by the ultrasonic liquid processor for 1.5 hours.

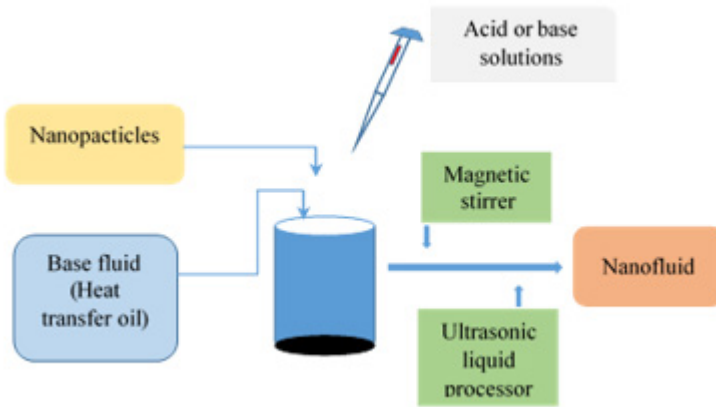


Figure 1. Nanofluid preparation scheme.

H_2SO_4 (sulphuric acid) and KOH (potassium hydroxide) solutions at 5 N (normality) valence were prepared to examine the effects on the stability values of the nanofluids. Each of the nanofluids with different mass ratios was added acid (H_2SO_4) and base (KOH) at volumetric ratios of 0% (base fluid), $10^{-3}\%$, $3.5 \times 10^{-3}\%$, $5.3 \times 10^{-3}\%$ and $8 \times 10^{-3}\%$ by using micropipette. Amounts of acid and base added were determined by measuring the pH variations of the deionized water. Figure 1 shows the pH variation of the H_2SO_4 acid solution at 5 N valence over deionized water. The selected acid and base percentage values are experimentally determined by comparison with deionized water. Measurements of pH were made with a digital pH meter. This device was calibrated with buffer solutions at pH values of 4 and 7 after each measurement.

Figure 2 shows the variation of pH in deionized water with the addition of volumetric percentages at 5 N (normality) valence of acid. The determined volu-

metric ratios of the acid and base were added directly into the base fluid after being directly mixed with the previously determined nanoparticle. After the addition, magnetic stirring was applied to the samples for about an hour. The same experiments were repeated four times for each sample. For each of the samples prepared with TiO_2 (titanium dioxide) and alumina (Al_2O_3) with mass ratios of 1%, 2% and 3%, the experiments were repeated four times for five different acids additives at the volumetric ratios of 0% (no additive), $10^{-3}\%$, $3.5 \times 10^{-3}\%$, $5.3 \times 10^{-3}\%$, $8 \times 10^{-3}\%$ and for five different base additives at the volumetric ratios of 0% (no additive), $10^{-3}\%$, $3.5 \times 10^{-3}\%$, $5.3 \times 10^{-3}\%$ and $8 \times 10^{-3}\%$.

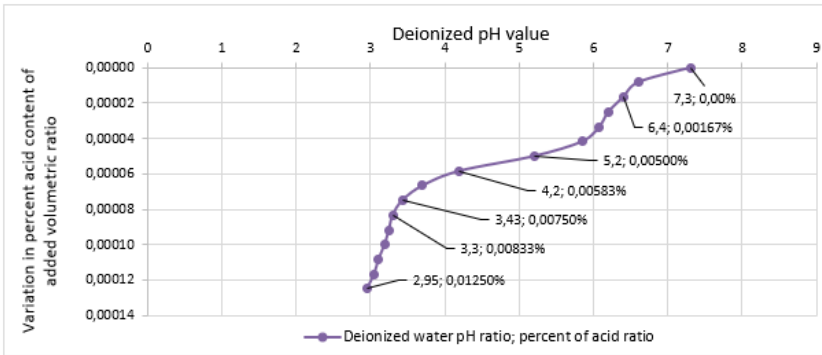


Figure 2. Variation of pH in deionized water with the addition of volumetric percentages of acid.

2.2. Sedimentation Method

The sedimentation method, zeta potential measurement method, UV-spectral analysis method, dynamic light scattering spectrometry method (DLS) and electron microscope measurement method (SEM, TEM) are the most frequently used methods in the literature to measure the stability of nanofluids [25].

The sedimentation method is one of the methods used to determine the stability values of nanofluids [26]–[28]. Sedimentation method is cheaper and useful method than others [29]. In order to use this method, it is necessary to make a colour difference in the sedimentation process between the nanoparticle and the basic fluid. There is a distinct colour difference between the alumina and titanium dioxide nanoparticles used in this study and the oil used as the base fluid.

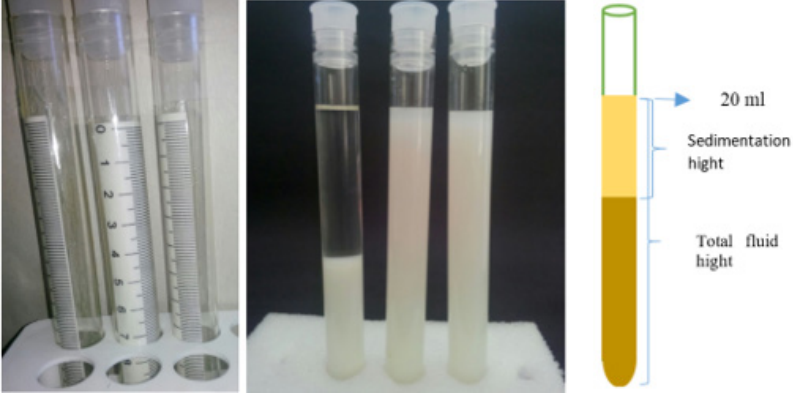


Figure 3. Sedimentation test samples and demonstration of measured areas.

As shown in Figure 3, after the nanofluids were prepared, about 20 ml of nanofluid were placed in the glass tubes and their mouths were closed. The time-lapse sedimentations were read from the scale created on the test tubes. The sedimentation altitude values taken at specific time intervals (the scale value of the light coloured zone in Figure 3) are recorded regularly. It is calculated that the resulting sedimentation value is equal to the total volume percent. Thereby, for selected nanoparticles, percent sedimentation values by time were calculated for the nanofluid produced using the mass fraction of the nanoparticle and the volumetric ratio of the acid or base solution. The samples were observed for about 36 hours. Average sedimentation percentages were determined at the end of 36 hours for each sample. Percent sedimentation rate was calculated by means of the following Equation 1. In Equation 1, PSR denotes percent sedimentation rate, SH denotes sedimentation height and TH denotes total fluid height. Each experiment was repeated four times and the averages of the values obtained were taken. The variation in these values by time is shown graphically in Figure 4 and Figure 5.

$$PSR = \frac{SH}{TH} \times 100 \quad (1)$$

The sedimentation characteristics of nanofluids are an important parameter for stability and are directly related each other. Low sedimentation values, a measure of the stability of the nanofluids, are required for good stability. The stability values of the nanofluids can be interpreted and compared according to the volume of the sedimentation in the nanofluids. The sedimentation values of the nanofluids prepared with acid and base at the specified ratios were compared with the sedimentation values of 0% acid-base (no additive) nanofluids. Then, the variation of stability values of nanofluids prepared with alumina and titanium dioxide nanoparticles on oil-basis was investigated by a sedimentation method.

2.3. Determination of Thermal Properties of Nanofluids

The thermal conductivities of the nanofluids were measured with KD2 Pro (Decagon Devices, Inc., USA). The KD2 Pro instrument is a device commonly used in literature to measure the thermal properties of fluids [15]–[18]. In the KD2 Pro instrument using the method of the transient line heat source, a KS-1 coded needle immersed in the fluid to be measured is used. Instantaneous power is given to the needle for a certain time, and then this tip is cooled in the fluid for a certain period. The thermal conductivity is calculated by using Equation 2 together with the instantaneous temperature/time variation of the device, and the calculated the thermal conductivity is read from the device screen.

$$k = \frac{q(\ln t_2 - \ln t_1)}{4\pi(\Delta T_2 - \Delta T_1)} \quad (2)$$

In Equation 2, q is the constant heat flux applied from the source, ΔT_1 and ΔT_2 are the instantaneous temperature differences, and t_1 and t_2 are the time difference.

Table 1. The basic properties of the nanoparticles and heat transfer fluids used

| Properties of the Material | Heat Transfer Oil | Al ₂ O ₃ (Alumina) | TiO ₂ (Titanium Dioxide) |
|--------------------------------------|-------------------|------------------------------------------|-------------------------------------|
| Density, ρ (kg/m ³) | 0.8551@ 22 °C | 3970 | 4000 |
| Thermal Conductivity, k (W/m K) | 0.128 | 40 | 11.7 |
| Particle size, (nm) | - | 20-30 | 30-40 |

The thermal conductivity and density values of the heat transfer oil given in Table 1 were determined experimentally. The values given in Table 1 of the nanoparticles were obtained from the relevant manufacturer. There are many experimental and theoretical methods in the literature regarding the measurement of the thermal conductivities of nanofluids. Since there are significant differences between the results of these methods, exact results cannot be obtained. In this study, the thermal conductivity values are determined by the classical models given in Table 2.

Table 2. Theoretical and experimental models in nanofluids

| Model | Reference | Year | Expression | Remark |
|--------------|----------------|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|
| Theoretical | Maxwell [30] | 1881 | $\frac{k_{eff}}{k_f} = \frac{k_p + 2k_f + 2\phi(k_p - k_f)}{k_p + 2k_f - \phi(k_p - k_f)}$ | Solid and Liquid Suspensions |
| Theoretical | Xue [30] | 2005 | $\frac{k_{eff}}{k_f} = \frac{1 - \phi + 2\phi \frac{k_p}{k_p - k_f} \ln \frac{k_p - k_f}{2k_f}}{1 - \phi + 2\phi \frac{k_f}{k_p - k_f} \ln \frac{k_p - k_f}{2k_f}}$ | Spheres Nanoparticles |
| Experimental | Timofeeva [31] | 2007 | $k_{NF} = (1 + 3\phi)k_f$ | Al ₂ O ₃ /Water Nanofluids |
| Experimental | Patel [32] | 2010 | $\frac{k_{eff}}{k_f} = 1 + 0.135 \left(\frac{k_p}{k_f}\right)^{0.273} \phi^{0.447} \left(\frac{T}{20}\right)^{0.537} \left(\frac{100}{d_p}\right)^{0.224}$ | Oxide/Water Nanofluids |

2.4. Uncertainty Analysis

In the experimental study, an uncertainty analysis was carried out to determine the magnitudes of the errors caused by the structure of the experiment set and measurement tools. Within the total uncertainty affecting the test results; measurements of thermal conductivity (k), thermal capacity (cp), mass (m) and volume (V) are the basic components in the experiments. It was accepted that there was no error caused by the manufacture of the instruments used in these measurements. Moreover, instruments having high accuracies were used in the experiment. However, the uncertainties for the measurements of the physical properties after the preparing nanofluids or before this stage are given in Table 3.

Table 3. Uncertainties of measurement values

| Property | Uncertainty (%) | Equipment Type |
|------------------------------------|-----------------|-------------------------|
| Thermal Conductivity, k | ±0.5 | KD2 Pro |
| Thermal Capacity (c _p) | ±0.5 | KD2 Pro |
| Mass (m) | ±0.2 | Digital Precision Scale |
| Volume (V) | ±0.287 | Variable Micro Pipette |

3. RESULTS AND DISCUSSION

3.1. Sedimentation Experiment Results

The acid and base additions were carried out at predetermined ratios for the nanofluids, which was prepared two-step method, containing nanoparticles of 1, 2 and 3% Al₂O₃ (Alumina) and 1, 2 and 3% TiO₂ (Titanium dioxide) by mass. Stability values of nanofluid samples containing nanoparticles at different fractions were determined by utilizing the percent sedimentation values measured by

the sedimentation method. For each sample, the experiments were repeated four times and the final values were determined by taking the average of the data obtained from the experiments. Unadulterated, i.e., containing 0% by volume of acid or base, samples were compared with nanofluid samples containing acid and base at different volumetric ratios. In Table 4, the percentage of sedimentation at the end of the sedimentation period of the nanofluids is given.

Acid and base solutions have been effective on the stability of the alumina nanofluid. In Figure 4, variations in acid-base-added sedimentation values of oil-based nanofluids with alumina nanoparticles of 1%, 2% and 3% by mass were given. As can be seen in Figure 4, it is possible to say that there is a linear relationship between the acid additions and the stability of the alumina nanofluids. When the alumina and acid-added nanofluids provided by the best stabilizers are examined, it can be seen that an acid content of $10^{-3}\%$ by volume for alumina of 1% by mass, an acid content of $3.5 \times 10^{-3}\%$ by volume for alumina of 2% by mass and an acid content of $8 \times 10^{-3}\%$ by volume for alumina of 3% by mass were found to be the best addition values. When the alumina-acid added nanofluids are examined, it has been determined that the highest stability improvement is a volume of $3.5 \times 10^{-3}\%$ acid for alumina at 2% by mass. In this latter case, it is clear from Table 4 that there is about 24% improvement in stability compared to that of the undoped (2% alumina and 0% acid) nanofluid. The lowest sedimentation rate was about 22.5% by volume for acid at 3% by mass and 8% by volume for alumina. Also, Figure 6 shows the effect of acid and base additives in volumetric ratios of $10^{-3}\%$, $3 \cdot 10^{-3}\%$, $5.3 \times 10^{-3}\%$ and $8 \times 10^{-3}\%$ on sedimentation values of oil-based nanofluids containing alumina at 1%, 2% and 3% of mass by time. In the absence of appropriate acid addition ratio values, it was found that the stability values of the acid-added nanofluids were worse than those of the non-additive (0% acid) nanofluids as shown in Figure 6.

Table 4. Percent of sedimentation at the end of the sedimentation period

| | | Sedimentation Values of Acid (H_2SO_4)-Base (KOH) Admixtures (%) | | | | | | | | | |
|-----------------------------|----|----------------------------------------------------------------------|-----------|----------------------|----------------------|--------------------|---------------------------------|-----------|----------------------|----------------------|--------------------|
| | | Volumetric Acid (H_2SO_4) Ratio (%) | | | | | Volumetric Base (KOH) Ratio (%) | | | | |
| | | 0 | 10^{-3} | 3.5×10^{-3} | 5.3×10^{-3} | 8×10^{-3} | 0 | 10^{-3} | 3.5×10^{-3} | 5.3×10^{-3} | 8×10^{-3} |
| Alumina Nanofluid | 1% | 58.5 | 52.6 | 62.125 | 63 | 66.125 | 58.5 | 33.25 | 40.25 | 29.5 | 50 |
| | 2% | 33.3 | 28.75 | 25.125 | 28 | 44.7 | 33.3 | 17.5 | 28 | 27.5 | 36 |
| | 3% | 34 | 29.5 | 27 | 28 | 22.5 | 34 | 34.5 | 34.5 | 30 | 33.5 |
| Titanium Dioxide Nanofluids | 1% | 44.25 | 75 | 100 | 100 | 100 | 44.25 | 59.25 | 64.25 | 100 | 100 |
| | 2% | 46 | 49 | 11.9 | 100 | 100 | 46 | 10.5 | 100 | 56.75 | 62.75 |
| | 3% | 28.25 | 7.15 | 100 | 100 | 100 | 28.25 | 100 | 8 | 100 | 100 |

Figure 4 shows the variation of acid and base-added sedimentation values of oil-based nanofluids containing alumina at 1%, 2% and 3% of mass by time.

The results of sedimentation experiments with nanofluids prepared with base additions and alumina nanoparticles were given in Figure 4. For the sedimentation values of alumina nanofluids, it was observed that base solutions were more effective than acid solutions. The best stability values or the lowest sedimentation values at mass ratios of 1%, 2% and 3% were obtained at base volume ratios of 5.3×10^{-3} %, 10^{-3} % and 5.3×10^{-3} %, respectively. The highest improvement in stability values with the addition of the base, relative to the undoped (0% base) nanofluid, was approximately 50% at 1% alumina by mass and at the base rate of 5.3×10^{-3} % by volume. As shown in Table 4, the lowest sedimentation value during the sedimentation test period is the volumetric ratio of 17.5% at 2% alumina by mass and at 10^{-3} % base by volume while it was found to be about 48% of the stability improvement compared to the unadulterated (2% alumina and 0% base) condition. In general, although different base additive rates have a positive effect on alumina nanofluids, the use of a base additive other than the appropriate values will cause the stability to deteriorate seriously, resulting in a rapid increase in sedimentation values, as it can be seen in 2% alumina by mass at a volumetric rate of 8×10^{-3} % base.

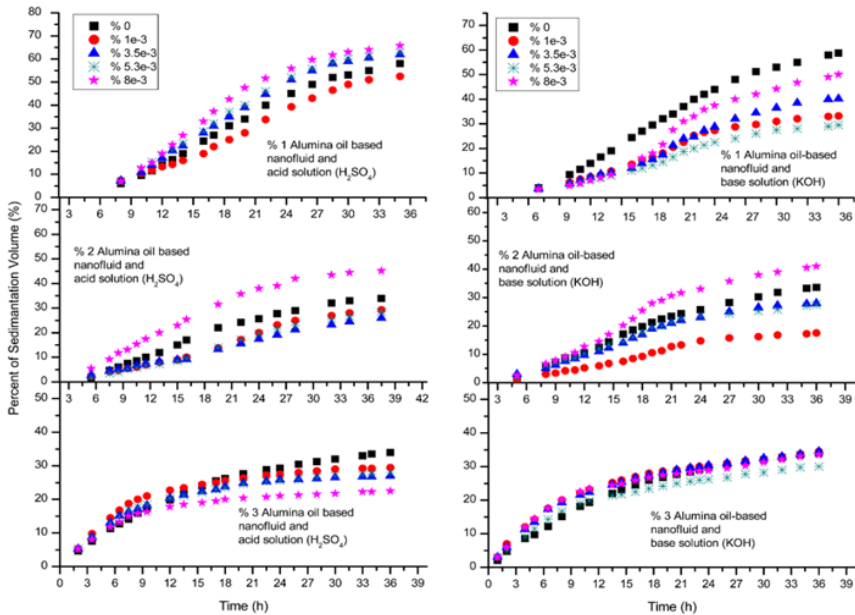


Figure 4. Variation of acid and base-added sedimentation values of oil-based alumina nanofluids by time.

Figure 5 shows the variation of acid and base-added sedimentation values of oil-based nanofluids containing titanium dioxide at 1%, 2% and 3% of mass by time. Also, Figure 7 shows the effect of acid and base additives in volumetric ratios

of $10^{-3}\%$, $3.5 \times 10^{-3}\%$, $5.3 \times 10^{-3}\%$ and $8 \times 10^{-3}\%$ on sedimentation values of oil-based nanofluids containing titanium dioxide at 1%, 2% and 3% of mass by time. In Figure 5 and Figure 7, the time-varying variations of the acid-base addition sedimentation values of oil-based nanofluids containing 1%, 2% and 3% of titanium dioxide in mass are given. Titanium dioxide nanoparticles have overreacted to acid and base additives. Some sedimentation values do not appear in Figure 5. The reason for this, the titanium dioxide nanofluids quickly collapsed by lumping in a short time after preparation. Within about 1-2 hours, all of the nanoparticles in the titanium dioxide nanofluids have collapsed.

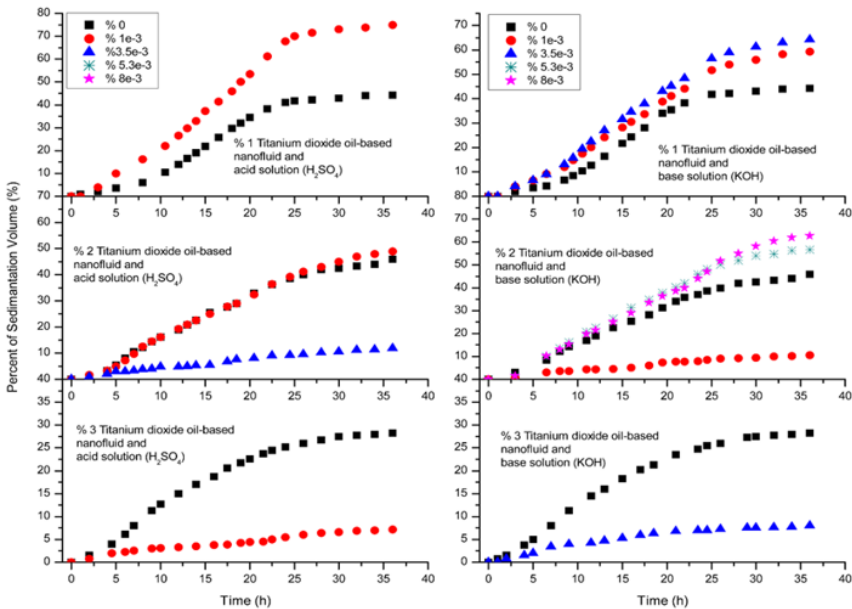


Figure 5. Variation of acid and base-added sedimentation values of oil-based titanium dioxide nanofluids by time.

As can be seen in Figure 5, when the sedimentation test results of nanofluids prepared with titanium dioxide and acid dopants are examined, it is determined that the ratio of acid suitable for 1% titanium dioxide in mass is not between selected acid values. Also, as can be seen in Figure 7, the stability values of the titanium dioxide-acid nanofluids generally worsen rapidly. However, in some titanium dioxide nanofluids and acid sedimentation experiments, high stability values, that is, low sedimentation values, have been reached. Compared to the nanofluids prepared without additives (at 0% acid ratio), stability improvements of 74% and 75% were obtained for titanium dioxide at mass ratios of 2% and 3%, respectively. As shown in Table 4, when the titanium dioxide and acid-added nanofluids were ta-

ken into account in the sedimentation test process, the lowest sedimentation values have been obtained excellent results at 12% and 7% for titanium dioxide at mass ratios of 2% and 3%, respectively.

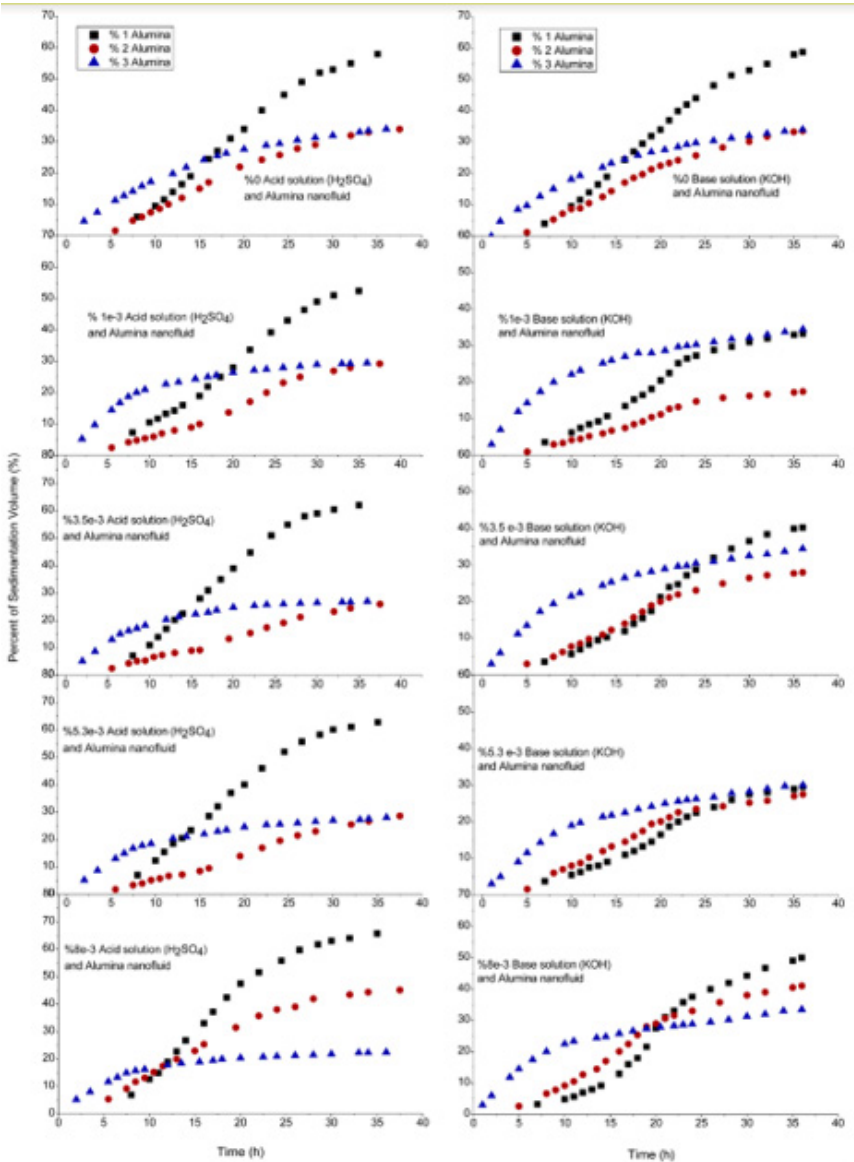


Figure 6. Effect of acid and base additives on sedimentation values of oil-based alumina nanofluids by time.

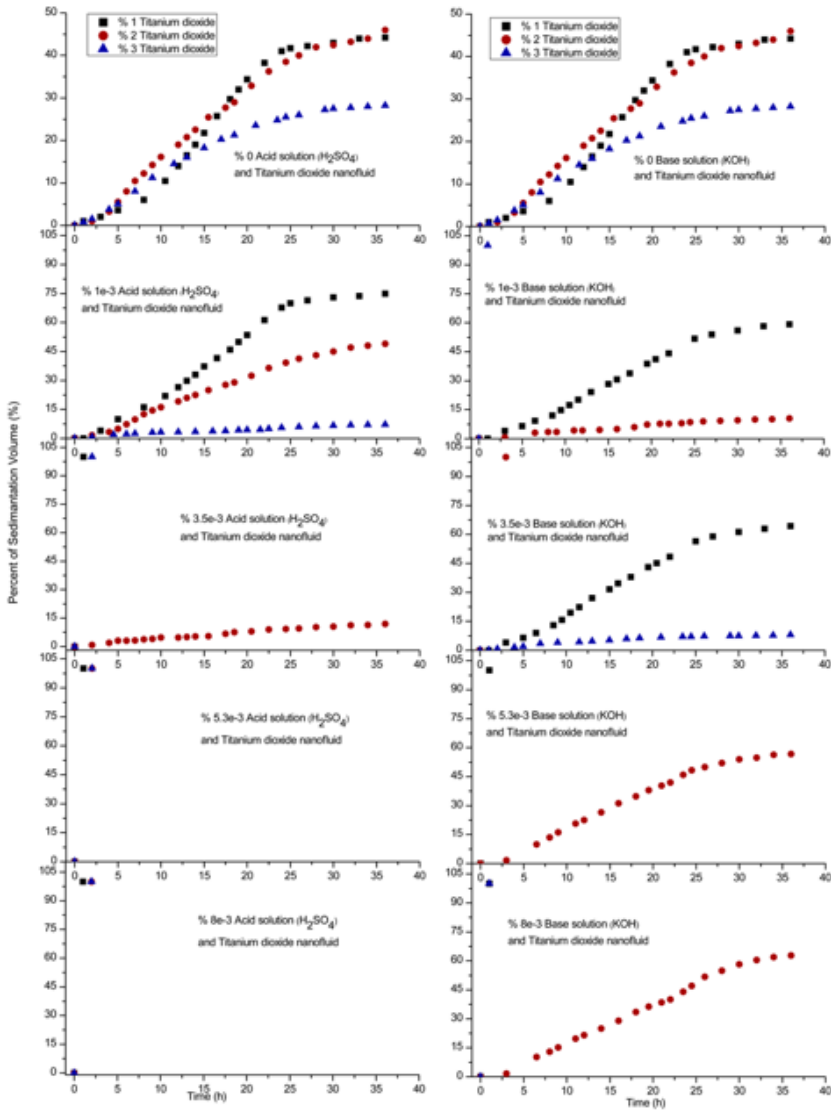


Figure 7. Effect of acid and base additives on sedimentation values of oil-based titanium dioxide nanofluids by time.

In base-added titanium dioxide nanofluids, suitable base ratios at a mass fraction of 1% could not be determined. However, high improvements in stability values for titanium dioxide at mass ratios of 2% and 3% were achieved. Stability improvements were achieved as the ratios of 77% and 72% at mass ratios of 2% and

3% for titanium dioxide at $10^{-3}\%$ and $3.5 \times 10^{-3}\%$ base ratios, respectively, relative to the sedimentation values of nanofluids without additive (0% base ratio). As can be seen in Figure 5 and Table 4, when the titanium dioxide and base-added nanofluids are taken into account in the sedimentation test process, the lowest sedimentation values have been obtained as the ratios of 10.5% and 8%, which is excellent results, for titanium dioxide at mass ratios of 2% and 3%, respectively.

3.2. Determination of Thermal Properties of Nanofluids

The thermal conductivities of alumina and titanium dioxide nanofluids were measured as a function of the variation in the mass proportions of the nanoparticles. Figure 8a shows the variations of the thermal conductivities of oil-based nanofluids containing alumina at 1%, 2% and 3% of mass compared to the base fluid (heat transfer oil). Figure 8b shows the variations of the thermal conductivities of oil-based nanofluids containing titanium dioxide at 1%, 2% and 3% of mass compared to the base fluid (heat transfer oil). Figure 8c shows the comparison of the variation of alumina nanofluid and the titanium dioxide nanofluid in the thermal conductivity. In Figure 8, the thermal conductivities of the nanofluids were given at about 20 °C according to the changing mass ratios (1%, 2% and 3%). It can be seen in Figure 8 that the thermal conductivity is clearly increased with the increase of the mass fraction. The values of the thermal conductivities of all the alumina and titanium dioxide nanofluids at the pre-determined ratios are higher than those of the base fluid, heat transfer oil, as shown in Figure 8c. It is possible to say that there is a linear relationship between the increasing mass ratios of the nanoparticles synthesized in the nanofluids and the thermal conductivities of these nanofluids. This result is similar to the literature [11], [31]–[33] no agreement has emerged about the mechanism of this phenomenon, or even about the experimentally observed magnitude of the enhancement. To address these issues, this paper presents a combined experimental and theoretical study of heat conduction and particle agglomeration in nanofluids. On the experimental side, nanofluids of alumina particles in water and ethylene glycol are characterized using thermal conductivity measurements, viscosity measurements, dynamic light scattering, and other techniques. The results show that the particles are agglomerated, with an agglomeration state that evolves in time. The data also show that the thermal conductivity enhancement is within the range predicted by effective medium theory. On the theoretical side, a model is developed for heat conduction through a fluid containing nanoparticles and agglomerates of various geometries. The calculations show that elongated and dendritic structures are more efficient in enhancing the thermal conductivity than compact spherical structures of the same volume fraction, and that surface [Kapitza]. Significant differences in the thermal properties of alumina and titanium dioxide nanofluids for the addition of acid and base solutions have not been measured. In the variation of thermal properties, the mass fraction was more decisive.

The comparison of the experimental and theoretical methods existing in the literature on the measurement of the thermal conductivities of the nanofluids with the experimental data obtained in this study is given in Figure 8. It has been found that the data obtained from the Maxwell theoretical model and the Timofeeva experimental model completely coincide and that the experimental data obtained from this study are also very close to these results. The data obtained from the theoretical models of Xue and Patel was found to increase rapidly with the increase of the mass mixing ratios and to move away from the results obtained from this study and from other theoretical and experimental data aforementioned.

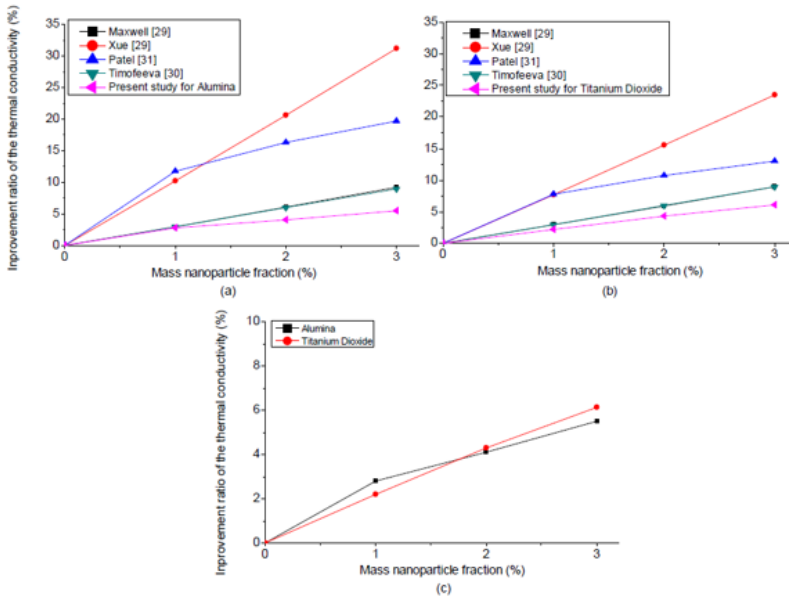


Figure 8. Variations of the thermal conductivities of oil-based nanofluids compared to the base fluid, (a) comparison of present study and theoretical models for alumina nanofluid, (b) comparison of present study and theoretical models for titanium oxide nanofluid, (c) increase in heat transfer coefficients of alumina and titanium oxide nanofluids

The variation of the thermal conductivities of alumina and titanium dioxide nanofluids with respect to the mass addition ratios is also given in Figure 8c. As can be seen in Figure 8c, the thermal conductivity of the titanium dioxide nanofluids at 2% and 3% by mass is generally higher than that of the alumina nanofluid. However, when the mass fraction of alumina is 1%, it is seen that the measured thermal conductivity value is higher than the same fraction of titanium dioxide. It has been assessed that the reason for this may be stability. This is because, when

sedimentation test results are examined in nanofluids prepared with 1% by mass of titanium dioxide nanoparticles, the stability values of titanium dioxide nanofluids for all acid and base values are not improved although significant improvements of the stability values with the same addition are obtained in all alumina nanofluids. When the sedimentation test results are examined in nanofluids containing 2% and 3% of nanoparticles in mass, much better results were obtained in the titanium dioxide nanofluids than in the alumina nanofluids.

4. CONCLUSIONS

In this study, the thermal characteristics of a heat transfer oil used in the industry have been tried to be improved by adding nanoparticles at certain mass ratios. Also, it was tried to contribute to experimental studies that nanofluids have limited oil-based studies. Numerous studies have been published in the literature on stability determination by means of pH and zeta potential measurements in nanofluids, where the base fluid is water. However, since the pH value cannot be measured in oil-based nanofluids, other methods should be used to determine the stability of the oil-based nanofluids. In this study, stability and thermal properties of alumina and titanium dioxide nanofluid were determined by a sedimentation method. In experimental studies conducted for this purpose, neutral surface loads of alumina and titanium dioxide nanoparticles gave significant responses in an acidic and basic oil environment. The stability which is a measure of the variation of the charge densities on the surface was measured by the sedimentation method and the most suitable values were determined in increasing acidic and basic environment. Accordingly, the highest rate of improvement in the stability values of the alumina nanofluids was about 50%, and for the titanium dioxide nanofluids, it was about 78%. The highest improvement in the thermal conductivity obtained with the alumina nanofluid was about 5.5%, while for titanium dioxide it was about 6.125%.

On the other hand, with this study, it was evaluated that studies on the stability of these nanofluids could be made by adding acid and base to oil-based nanofluids at a certain rate. In order to achieve higher stability values by using this method in oil-based nanofluids, it is evaluated that different studies can be performed to take account of acid or base values at different normality values and addition ratios.

Author Contribution Rates :

Design of Study: FŞ (%50), LN (%50)

Data Acquisition: FŞ (%100)

Data Analysis: FŞ (%60), LN (%40)

Writing Up: FŞ (%70), LN (%30)

Submission and Revision: FŞ (%95), LN (%5)

REFERENCES

- A. A. Adekunle ve S. O. Oparanti, "A Review on Physicochemical and Electrical Performance of Vegetable Oil-Based Nanofluids for High Voltage Equipment", *Electric Power Systems Research*, c. 214, s. 108873, Oca. 2023, doi: 10.1016/j.epsr.2022.108873.
- A. Ghadimi, R. Saidur, ve H. S. C. Metselaar, "A review of nanofluid stability properties and characterization in stationary conditions", *International Journal of Heat and Mass Transfer*, c. 54, sayı 17-18, ss. 4051-4068, 2011, doi: 10.1016/j.ijheatmasstransfer.2011.04.014.
- A. Menbari, A. A. Alemrajabi, ve Y. Ghayeb, "Experimental investigation of stability and extinction coefficient of Al₂O₃-CuO binary nanoparticles dispersed in ethylene glycol-water mixture for low-temperature direct absorption solar collectors", *Energy Conversion and Management*, c. 108, ss. 501-510, 2016, doi: 10.1016/j.enconman.2015.11.034.
- A. Menbari, A. A. Alemrajabi, ve Y. Ghayeb, "Investigation on the stability, viscosity and extinction coefficient of CuO-Al₂O₃/Water binary mixture nanofluid", *Experimental Thermal and Fluid Science*, c. 74, ss. 122-129, 2016, doi: 10.1016/j.exptthermfluidsci.2015.11.025.
- Babita, S. K. Sharma, ve S. M. Gupta, "Preparation and evaluation of stable nanofluids for heat transfer application: A review", *Experimental Thermal and Fluid Science*, c. 79, ss. 202-212, Ara. 2016, doi: 10.1016/j.exptthermfluidsci.2016.06.029.
- B. Mehta, D. Subhedar, H. Panchal, ve Z. Said, "Synthesis, stability, thermophysical properties and heat transfer applications of nanofluid - A review", *Journal of Molecular Liquids*, c. 364, s. 120034, Eki. 2022, doi: 10.1016/j.molliq.2022.120034.
- D. K. Devendiran ve V. A. Amirtham, "A review on preparation, characterization, properties and applications of nanofluids", *Renewable and Sustainable Energy Reviews*, c. 60, ss. 21-40, 2016, doi: 10.1016/j.rser.2016.01.055.
- E. V. Timofeeva vd., "Thermal conductivity and particle agglomeration in alumina nanofluids: Experiment and theory", *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, c. 76, sayı 6, 2007, doi: 10.1103/PhysRevE.76.061203.
- F. Sahin ve L. Namlı, "Nanoakışkanlarda Kararlılığın Isı Transferini İyileştirme Açısından Önemi", *Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi*, c. 7, sayı 2, ss. 880-898, Tem. 2018, Erişim: Eyl. 10, 2018. [Çevrimiçi]. Available at: <https://dergipark.org.tr/tr/download/article-file/509103>.
- G. D. Xia, R. Liu, J. Wang, ve M. Du, "The characteristics of convective heat transfer in microchannel heat sinks using Al₂O₃ and TiO₂ nanofluids", *International Communications in Heat and Mass Transfer*, c. 76, ss. 256-264, 2016, doi: 10.1016/j.icheatmasstransfer.2016.05.034.
- G. Humnic ve A. Humnic, "Application of nanofluids in heat exchangers: A review", *Renewable and Sustainable Energy Reviews*, c. 16, sayı 8, ss. 5625-5638, 2012, doi: 10.1016/j.rser.2012.05.023.
- G. Xia, H. Jiang, R. Liu, ve Y. Zhai, "Effects of surfactant on the stability and thermal conductivity of Al₂O₃/de-ionized water nanofluids", *International Journal of Thermal Sciences*, c. 84, ss. 118-124, 2014, doi: 10.1016/j.ijthermalsci.2014.05.004.
- H. Chang ve M. Kao, "An Innovative Nanofluid Manufacturing System", *Society*, c. 28, sayı 2, ss. 187-193, 2007.

- H. Chang ve S.-C. Lin, "Fabrication Method for a TiO₂ Nanofluid with High Roundness and Superior Dispersion Properties", *Materials Transactions*, c. 48, sayı 4, ss. 836–841, 2007, doi: 10.2320/matertrans.48.836.
- H. E. Patel, T. Sundararajan, ve S. K. Das, "An experimental investigation into the thermal conductivity enhancement in oxide and metallic nanofluids", *Journal of Nanoparticle Research*, c. 12, sayı 3, ss. 1015–1031, 2010, doi: 10.1007/s11051-009-9658-2.
- H. Lin vd., "Recent advances in thermal conductivity and thermal applications of graphene and its derivatives nanofluids", *Applied Thermal Engineering*, c. 218, s. 119176, Oca. 2023, doi: 10.1016/j.applthermaleng.2022.119176.
- H. Karimian ve A. A. Babaluo, "Halos mechanism in stabilizing of colloidal suspensions: Nanoparticle weight fraction and pH effects", *Journal of the European Ceramic Society*, c. 27, sayı 1, ss. 19–25, 2007, doi: 10.1016/j.jeurceramsoc.2006.05.109.
- H. Zhu, C. Zhang, Y. Tang, J. Wang, B. Ren, ve Y. Yin, "Preparation and thermal conductivity of suspensions of graphite nanoparticles", *Carbon*, c. 45, sayı 1, ss. 226–228, 2007, doi: 10.1016/j.carbon.2006.07.005.
- L. Yang, K. Du, X. Niu, Y. Li, ve Y. Zhang, "An experimental and theoretical study of the influence of surfactant on the preparation and stability of ammonia-water nanofluids", *International Journal of Refrigeration*, c. 34, sayı 8, ss. 1741–1748, 2011, doi: 10.1016/j.ijrefrig.2011.06.007.
- M. A. Khairul, K. Shah, E. Doroodchi, R. Azizian, ve B. Moghtaderi, "Effects of surfactant on stability and thermo-physical properties of metal oxide nanofluids", *International Journal of Heat and Mass Transfer*, c. 98, ss. 778–787, 2016, doi: 10.1016/j.ijheatmasstransfer.2016.03.079.
- M. Hemmat Esfe, A. Karimipour, W. M. Yan, M. Akbari, M. R. Safaei, ve M. Dahari, "Experimental study on thermal conductivity of ethylene glycol based nanofluids containing Al₂O₃ nanoparticles", *International Journal of Heat and Mass Transfer*, c. 88, ss. 728–734, 2015, doi: 10.1016/j.ijheatmasstransfer.2015.05.010.
- M. Raja, R. Vijayan, P. Dineshkumar, ve M. Venkatesan, "Review on nanofluids characterization, heat transfer characteristics and applications", *Renewable and Sustainable Energy Reviews*, c. 64, ss. 163–173, 2016, doi: 10.1016/j.rser.2016.05.079.
- M. J. Muhammad, I. A. Muhammad, N. A. C. Sidik, M. N. A. W. M. Yazid, R. Mamat, ve G. Najafi, "The use of nanofluids for enhancing the thermal performance of stationary solar collectors: A review", *Renewable and Sustainable Energy Reviews*, c. 63, ss. 226–236, 2016, doi: 10.1016/j.rser.2016.05.063.
- S. A. Simakov ve Y. Tsur, "Surface stabilization of nano-sized titanium dioxide: Improving the colloidal stability and the sintering morphology", *Journal of Nanoparticle Research*, c. 9, sayı 3, ss. 403–417, 2007, doi: 10.1007/s11051-006-9099-0.
- S. U. S. Choi, Z. G. Zhang, W. Yu, F. E. Lockwood, ve E. A. Grulke, "Anomalous thermal conductivity enhancement in nanotube suspensions", *Applied Physics Letters*, c. 79, sayı 14, s. 2252, Eyl. 2001, doi: 10.1063/1.1408272.
- S. M. S. Murshed, K. C. Leong, ve C. Yang, "Enhanced thermal conductivity of TiO₂ - Water based nanofluids", *International Journal of Thermal Sciences*, c. 44, sayı 4, ss. 367–373, 2005, doi: 10.1016/j.ijthermalsci.2004.12.005.
- S. (Sadık) Kakaç, "Heat transfer enhancement of heat exchangers", s. 676, 1999.
- S. M. S. Murshed, K. C. Leong, ve C. Yang, "Thermophysical and electrokinetic properties of nanofluids - A critical review", *Applied Thermal Engineering*, c. 28, sayı 17–18, ss. 2109–2125, 2008, doi: 10.1016/j.applthermaleng.2008.01.005.
- S. Kakaç ve A. Pramuanjaroenkij, "Review of convective heat transfer enhancement with nanofluids", *International Journal of Heat and Mass Transfer*, c. 52, sayı 13–14, ss. 3187–3196, 2009, doi: 10.1016/j.ijheatmasstransfer.2009.02.006.
- S. U. Ilyas, R. Pendyala, ve N. Marneni, "Preparation, sedimentation, and agglomeration of nanofluids", *Chemical Engineering and Technology*, c. 37, sayı 12, ss. 2011–2021, 2014, doi: 10.1002/ceat.201400268.
- Y. Xuan ve Q. Li, "Heat transfer enhancement of nanofluid", c. 21, sayı February 2000, ss. 58–64, 1999, doi: 10.1016/S0142-727X(99)00067-3.
- X. Li, D. Zhu, ve X. Wang, "Evaluation on dispersion behavior of the aqueous copper nano-suspensions", *Journal of Colloid and Interface Science*, c. 310, sayı 2, ss. 456–463, 2007, doi: 10.1016/j.jcis.2007.02.067.
- W. Yu, H. Xie, Y. Li, L. Chen, ve Q. Wang, "Experimental investigation on the heat transfer properties of Al₂O₃nanofluids using the mixture of ethylene glycol and water as base fluid", *Powder Technology*, c. 230, ss. 14–19, 2012, doi: 10.1016/j.powtec.2012.06.016.