Experimental investigation on the thermal conductivity of Triethylene Glycol-Water-CuO nanofluids as a desiccant for dehydration process

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Abstract
Liquid desiccants such as glycols are used in dehydration process, among which Triethylene Glycol (TEG) is considered as a common choice. The addition of nanoparticles to TEG as the base fluid is one of the prevalent method to improve thermal properties of TEG. In this study, an experimental investigation was performed on thermal conductivity of TEG-based nanofluids with 20 and 40 nm diameter copper oxide (CuO) nanoparticles analyzed at different conditions. Thermal conductivity was measured using a Decagon thermal analyzer (KD 2 Pro Model) in the 20 °C-60 °C temperature range, and also 0.1- 0.9 wt.% range. The experimental results showed that thermal conductivity of the nanofluid enhances with temperature increasing. In addition, thermal conductivity of nanofluids increased with nanoparticle concentration in both cases of 20 and 40 nm nanoparticles. The highest enhancement was also ~ 13.5%, for the nanofluid with 20 nm nanoparticles at 60 °C and a 0.9 wt.% concentration.

Keywords: CuO Nanoparticle; Dehydration; Nanofluid; Thermal Conductivity; Triethylene Glycol.

INTRODUCTION
Natural gas (NG) entering into the gas processing plants often carries large amounts of water vapor commonly near saturation conditions. The presence of water vapor in the gas stream leads to serious problems during gas transportation and treatment such as hydrate formation, corrosion (especially in the presence of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \)), reduction of line capacity due to accumulation of free water and reduction of heating value [1]. Various techniques are commonly used for the production of high quality gas with the least possible water content, among which absorption is considered as the most attractive from economical point of view and it has been practiced in industrial scale for years [1]. In case that dew point depression should be in the order of 15-49 °C, glycols are commonly used. Among various glycols such as monoethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TREG), TEG has been the most common selection for NG dehydration [2].

However, the regeneration of TEG-water mixtures is necessary for reuse, entailing high temperatures in the recovery process. As a result, improvement of thermal properties like thermal conductivity leads to the reduction of heat requirements for TEG-water separation which in turn improves the quality of regenerated TEG. Rich
TEG has water contents ~ 2-5 wt.% which should be regenerated at 204 °C to produce lean TEG with water contents <0.5 wt.%, which is nearly pure making regeneration requirements very intense.

Nanofluids are considered as a new-generation of heat transfer fluids as they propose new possibilities to enhance heat transfer properties compared with pure heat transfer fluids [3, 4]. Nanofluids, consisting of solid nanoparticles in the 1-100 nm size range, have drawn serious attention due to superior properties in comparison with conventional heat transfer fluids [5-9]. They exhibit high thermal conductivities compared with traditional coolants making them suitable for heat transfer applications. Small nanoparticle contents with uniform dispersion can bring about significant improvements in thermal properties of the base fluid [10,11].

Various nanoparticle materials including metallic, non-metallic and polymeric can be added into the base fluids, which are expected to enhance the thermal conductivity higher than base fluids. An industrial application test was carried out by Liu et al. [12] and Ahuja [13], in which the effects of particle vol.%, size, pressure drop and thermal properties were investigated. In such cases, the suspended particles are of μm or even mm dimensions. Such large particles may cause severe problems such as abrasion and clogging; thus large suspended particles may be of little practical use in heat transfer enhancement [14].

Choi [15] was the first who coined the term nanofluids to refer to the fluids with suspended nanoparticles. Some preliminary experimental results [16] showed that ~ 60% enhancement in thermal conductivity can be obtained for a nanofluid consisting of water and 5 vol.% CuO nanoparticles [14]. Various nanoparticles have been utilized to improve fluid thermal properties, with the most prevalent as metal and metal oxide nanoparticles [17]. Metal oxides such as alumina (Al₂O₃) [18, 19], copper oxide (CuO) [19, 20], magnetite (Fe₃O₄) [21, 22], zinc oxide (ZnO) [19, 23], titania (TiO₂) [24, 25] and silica (SiO₂) [26, 27] have been used and reported.

Das et al. [28] investigated thermal characteristics of nanofluids containing Al₂O₃ & CuO nanoparticles in water as the base fluid. Nanoparticles have been 38.4 and 28.6 nm in size, respectively. They measured the thermal conductivity of nanofluids with nanoparticle concentrations at 1 & 4 vol.% in the 21-51 °C temperature range. At 4 vol.%, the highest increase in thermal conductivity was observed to be 24 and 36%. The thermal properties of Al₂O₃ & ZnO nanoparticles, suspended in a MEG-water mixture were investigated by Kim et al. [29]. The particle volume fraction is varied from 0.3 to 3% and 0.1 to 3%, at 20 °C. Based on the results, thermal conductivity is increased by increasing the nanoparticle volume fraction. The maximum enhancement was 11 and 21%, respectively.

Li & Peterson [30], studied the thermal conductivity of Al₂O₃·H₂O and CuO·H₂O nanofluids. Nanoparticle volume fraction was varied in the 2-6% and 2-10% ranges at temperatures between 28 °C to 34 °C. The results showed that the maximum enhancement was 29 and 51%, respectively. Beck et al. [31] reported the thermal conductivity of nanofluids with Al₂O₃ nanoparticles dispersed in water and MEG with 1.86 to 4 vol.% and 2 to 3.01% at room temperature. The results indicated that the thermal conductivity is increased as particle concentration is enhanced. Vajjha & Das [32], investigated the effect of Al₂O₃ & CuO nanoparticles on the thermal conductivity of a MEG-water mixture as the base fluid. The nanoparticles sizes were 53 and 29 nm, respectively. Nanoparticle volume fraction was varied between 0-10% and 0-6% at temperatures in the 25-90 °C range. The maximum enhancements were 69 and 60%. Shima et al. [33], investigated the thermal conductivity of nanofluids with Fe₃O₄ nanoparticles in oil as the base fluid at 25 °C. Volumetric concentrations were between 1 and 5.5 vol.%. The largest enhancement was 25%. Mintsa et al. [34], reported the enhanced thermal conductivity in comparison with water as the base fluid and investigated the variation of thermal conductivity of nanofluids with 47 nm alumina and 29 nm CuO nanoparticles. The largest enhancement values were 31 and 24% at a 20-48 °C temperature range. Turgut et al. [35] investigated the thermal properties of nanofluids mixed with water as the base fluid with TiO₂ nanoparticles. Effect of different concentrations between 0.2 and 3 vol.% was investigated. The results showed that thermal conductivity is increased by increasing nanoparticle concentration and the highest enhancement was 7.4% in a 13-55 °C temperature range. Sabbaghi and Sahooli [20], investigated the thermal conductivity of nanofluids with CuO nanoparticles in MEG as the base fluid at a temperature range of 25-90 °C. Volumetric concentrations were between 0.01
and 1 vol.%. The highest enhancement was 58%. According to the results, increasing nanoparticle concentration leads to an increase in the nanofluid thermal conductivity.

Recently, Esfe et al. [36] studied thermophysical properties such as thermal conductivity and viscosity of the Fe-water nanofluids. The effect of different nominal diameters of nanoparticles and concentrations on the thermal conductivity and viscosity was examined. Afrand et al. [37] investigated the effects of temperature and nanoparticle concentration on the rheological behavior of Fe$_3$O$_4$-Ag/EG hybrid nanofluids. Moreover, Afrand et al. [38] studied the thermal conductivity of Fe$_3$O$_4$ magnetic nanofluids. Nanofluid samples were prepared with volume fractions of 0.1%, 0.2%, 0.4%, 1%, 2% and 3%. Nasajpour et al. [39] investigated the effect of volume fraction (0.125-2%) and temperature (25-50 °C) on the thermal conductivity of ZnO–Ag (50%-50%) water-based nanofluids.

While many studies have been conducted on the effect of nanoparticles on thermal conductivity of different nanofluids (mainly on water and MEG based nanofluids), TEG has not been studied as the base fluid in spite of its extensive industrial applications. This study was performed to investigate the thermal conductivity of nanofluids with 20 and 40 nm diameter CuO nanoparticles in TEG as the common liquid desiccant in gas dehydration. The experiments were performed at 20 °C up to 60 °C, while particle concentration range varied between 0.1 wt.% and 0.9 wt.%. SEM, TEM and PSA analyses were performed for characterization of nanoparticles and the prepared nanofluids. Also, the experimental results for thermal conductivity were compared with other experimental outcomes and models reported in previous studies.

MATERIALS AND METHODS

TEG, CuO nanoparticles, Triton X-100 and Tetra ethyle amonium hydroxide used in this study, were of analytical grade purchased from Merck Co. (Germany), US Research Nanomaterials Co. (USA), Molekula Co. (UK) and Merck Co., respectively. To ensure well dispersion and particle size distribution, NANO-flex microtrac DLS was used. Thermal conductivity was measured using KD$_2$ Pro Decagon device at various temperatures.

Actually, the KD$_2$ Pro Decagon device applied the transient hot wire (THW) method for evaluation of the thermal conductivity of different fluids established itself as the most accurate, reliable and robust technique. It was introduced instead of the steady-state methods primarily because of the difficulty to determine that steady state conditions have indeed been established and for fluids the difficulty to eliminate the occurrence of natural convection. The method consists in principle of determining the thermal conductivity of considered fluid by observation the rate at which the temperature of device sensor increases with time after a step change in voltage is applied to it [40]. THW measures the thermal conductivity of nanofluids by prompt measurement of temperature of a thin platinum or titanium wire possessing diameter of 5-80 m during increasing applied voltage by passing the time. KD$_2$ Pro Decagon device utilizes a stainless steel needle sensor having 60 mm long and a 1.27 mm diameter (KS-1) based on the ASTM D5334 and IEEE 442-1981 standards, where the needle sensor is put in the nanofluid container perpendicularly and for maintenance the temperature constant, nanofluids container is put in a constant temperature steady state water bath circulating water continuously [41,42]. The properties and error of the needle sensor applied in this research are given briefly in Table 1. Firstly, the KS-1 needle sensor was calibrated and validated by conducting initial test for thermal conductivity measurement of glycerin. The thermal conductivity value equaled 0.285 W/m.K with a ±0.3% precision. Besides, in order to validate and ensure the accuracy of the obtained results error analysis was done. For this purpose, thermal conductivity of pure water was measured and compared with reference data [43] at a 20-

<table>
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<tr>
<th>Sensor Model</th>
<th>Single needle (KS-1)</th>
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<tr>
<td>Diameter</td>
<td>1.3 mm</td>
</tr>
<tr>
<td>Length</td>
<td>60 mm</td>
</tr>
<tr>
<td>Range</td>
<td>0.10 to 4.00 W/(m·K)</td>
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<tr>
<td>Accuracy</td>
<td>±10% from 0.2 - 4 W/(m·K)</td>
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<tr>
<td></td>
<td>±0.02 W/(m·K) from 0.1 - 0.2 W/(m·K)</td>
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60 °C temperature range with 10 °C intervals. The outcomes revealed that there was a 2% error bar for estimation of thermal conductivity by KD2 Pro device and the deviation from the reference values was approximately 2%. In order to measure the thermal conductivity correctly, a 50 ml volume of the sample was required. Furthermore, the setup had three major equipment including thermal conductivity analyzer, heating-cooling water bath and ultrasonic stabilizer. To ensure the accuracy and minimize the possible error of the obtained outcomes, all measurements repeated three times with a 20 min time interval at each temperature and the average values were reported.

Nanoparticles Morphology

Fig. 1 illustrates SEM and TEM analyses of 20 and 40 nm commercial nanoparticles, carried out by Iranian Nanomaterials Pioneers Company; approve the spherical morphology of the applied nanoparticles. These figures reveal that the powders consist of spherical particles with a regular morphology and narrow size distribution. The sizes of the particles observed in the images are in a range of 20 and 40 nm.

Preparation of Nanofluids

Preparation of stable nanofluids is the first key step in the experimental study of nanofluid properties. Nanofluids should possess special properties including stable and durable suspensions, negligible agglomeration and no chemical variation.

A two-step method is commonly used for synthesis of nanofluids [3]. In this method, nanoparticles are first produced or prepared from available commercial nanopowders and then dispersed in the desired base fluid. Generally, ultrasonication is used to improve particle dispersion and reduce agglomeration [3], which was applied in this study.

Two types of CuO nanoparticles with average diameters of 20 and 40 nm were dispersed into the base fluid composed of equal volume percent of TEG and water with varying nanoparticle weight percent from 0.1 to 0.9% with a 0.2% interval.
Triton X-100 (TX-100) and tetraethyleamonium hydroxide (TEAOH) 40% in water were added 0.24 mM (equal to its critical micelle concentration) and 1 vol.% respectively as surfactants to stabilize TEG-water and pure TEG nanofluids during more than ten and five days, respectively. Ultrasonication was also used to enhance the stability of nanofluids. A mixture of base fluid and nanoparticles was stirred on a magnetic stirrer for 10 min before being subjected to ultrasonication. Finally, nanofluids were ultra-sonicated for 20 min under 200w intensity. Generally, there are three techniques for assessing the stability of nanofluids including continuous observation during the time, zeta potential analyzer and UV–Vis spectrophotometer [44]. In this study, two methods of observation and zeta potential analysis were used. Figs. 2 (a-d) show the TEG-water based nanofluid contained TX-100 on the first day, on the next day, during a 10-day period and within two weeks, respectively. Furthermore, Figs. 2 (e-g) depict pure TEG based nanofluid contained TEAOH on the first day (e), on the next day (f) and during a 3-day period (g).

As can be seen in figures, there is no significant deposition during the initial days. Moreover, Fig. 3 demonstrates the zeta potential results for applied nanofluids. In order to investigate the stability of the nanofluids, the zeta potential and pH of the nanofluids applied in this study were measured and compared with the pH of the point that has zeta potential equal to zero (PZC) which is the most unstable point of nanofluids with zero interfacial charge density on nanoparticles. For this purpose, several drops of ammonia solution were added to the nanofluids in order to change the pH value to find the PZC of the samples. As shown in Fig. 3, the zeta potential values are given vs. various pH. The significant difference between pH of applied nanofluids in this study with zeta potential of 40 mV approximately and pH of the point of zero charge (PZC) revealed the stability of prepared nanofluids.

Particle Size Analysis
To investigate the effect of particle size on thermal conductivity of nanofluid, two types of...
of nanoparticles with 20 and 40 nm average diameters were used. DLS was used for determination of particle size distribution in the nanofluids and the results were presented in Figs. 4a and 4b. DLS results show that the desirable particle size was obtained when nanoparticles were suspended to the base fluid. These figures show that nanoparticles with 20 and 40 nm size are approximately monodispersed.

RESULTS AND DISCUSSION

In order to study the effect of nanoparticles on the thermal conductivity of water and TEG, temperature and concentration of nanoparticles were selected as the effective parameters. The results were also summarized in the following sections.

Effect of temperature

In order to investigate the effect of temperature on nanofluid thermal conductivity, 0.5 wt.% nanofluids with two different sizes were prepared. The base fluid was a TEG-water mixture with equal volume fractions of water and TEG. Fig. 5 shows that thermal conductivity of both nanofluids is higher than the base fluid at all temperatures. The figure also reveals that thermal conductivity of all nanofluids increases with temperature. The thermal conductivity of both pure base fluids based on temperature effect are presented in Fig. 6 (Dow Chemical Company, Union Carbide Corporation, Triethylene glycol product guide). It is obvious in Fig. 6 that TEG thermal conductivity decreases with temperature, while thermal conductivity of water increases with temperature. Therefore, the trend of thermal conductivity of TEG-water mixture in Fig. 5 can be attributed to effect of thermal conductivity of pure water and nanoparticles addition.

Effect of nanoparticle concentration

Nanoparticle concentration (wt.%) is another

![Figure 4(a)](image)

(a)

![Figure 4(b)](image)

(b)

Fig. 4. PSA of the nanofluid with (a) 20 nm average size, (b) 40 nm.
parameter affecting nanofluid thermal conductivity. Both Figs. 7 and 8 show the effect of concentration on two types of nanofluids with different nanoparticle concentration. The results represented that both nanofluids were dependent on nanoparticle concentration where the enhancement of thermal conductivity is maximum for the highest value of concentration.

It is clear that the inter-particle distance decreased by increasing the nanoparticle concentration. At higher concentrations, particle to particle interaction increased resulting in enhancement of thermal conductivity [20, 45].

Effect of the base fluid

In order to investigate the base fluid effect, two samples of TEG containing 20 and 40 nm CuO nanoparticles at 0.5 wt.% were prepared. These samples were assessed for their thermal conductivity at various temperatures given in Figs. 9 and 10 and compared with water-TEG based nanofluids.

The thermal conductivity enhancement for CuO-TEG-water nanofluid was found to be larger than that of CuO-TEG nanofluid. The best possible explanation is the difference in viscosity of the two fluids. Lower-viscosity values permit particles to interact more rapidly, leading to increasing the Brownian motion. This, in turn, leads to more strong inter-particle interactions.

Another reason could be attributed to the interfacial properties of the particle and base fluid. Interfacial effects have been shown to enhance the thermal conductivity of nanofluids. For

![Fig. 5. Thermal conductivity for 0.5 wt.% nanofluids at various temperatures.](image)

![Fig. 6. Thermal conductivity for pure water and pure TEG at various temperatures [43].](image)
Fig. 7. Thermal conductivity value for various nanofluid concentrations at 60 °C.

Fig. 8. Thermal conductivity enhancement for various nanofluid concentrations at 60 °C.

Fig. 9. Thermal conductivity of pure TEG and 20 nm, 0.5 wt.% samples at various temperatures.
example, the thermal conductivity of a nanofluid is influenced by a molecular-level layering of the fluid at the solid interface [45, 46]. The atomic structure of the liquid at the nanoparticle surface is much more ordered than that of the liquid in the bulk. It is the ordered nature of this layer that permits a higher thermal conductivity when compared to the randomly oriented fluid in the bulk. The ordered layer of fluid molecules can be represented as an interfacial shell, within which energy is efficiently transferred through phonons. Thickening of this shell results in a corresponding increase in the interfacial volume leading to higher heat conduction capacity [47]. The viscosity of the fluid and the interfacial properties of the particle-fluid interface both affect the thermal conductivity of nanofluids [48, 49]. Considering these mechanisms, it can be concluded that the thermal conductivity and/or thickness of the interfacial shell in the CuO-TEG-water system is larger than that of CuO-TEG. Consequently, the effect of CuO nanoparticle on thermal conductivity enhancement is greater for TEG-water suspensions than that of suspensions of pure TEG.

As known, although nanoparticle addition can promote thermal conductivity of base fluids, it may increase nanofluids viscosity that leads to pressure drop, subsequently. In order to investigate this controversial effect, the viscosity values were determined in previous studies [50,51]. According to the viscosity results, it was shown that increasing the particle size increases the viscosity. Therefore,
in order to use nanoparticles for thermal property enhancement, smaller particles should be selected to reduce pressure drop and the pumping power. Moreover, increasing the concentration of nanoparticles, results in viscosity enhancement. For thermal enhancement applications, an economically optimal concentration must be selected. The highest viscosity enhancement occurs for 40 nm nanoparticles at a 0.9 wt.% concentration at 75 °C that was about 19%. As a result, according to obtained results for thermal conductivity, the viscosity enhancement of the sample that has had the best performance is not problematic, undoubtedly.

Furthermore, the addition of surfactant may increase the thermal conductivity of nanofluids, although this enhancement has not been considered. In fact, because of the thermal conductivity of surfactant has smaller order (in range of base fluid) compared with solid metal oxide nanoparticles, this enhancement was considered negligible.

The enhancement of thermal conductivity at various temperatures is summarized in Fig.11. Besides, thermal conductivity enhancements for all samples of nanofluids are indicated in Table 2. The highest values at 60 °C are 6.767 % and 4.88 % for 20 nm and 40 nm nanoparticles, respectively. The viscosity decreased by temperature and lower viscosity at higher temperatures permits particles to move rapidly which intensifies Brownian motion [45]. In addition, due to the small size of the particles, additional energy transport can arise from the motions induced by stochastic (Brownian) and inter-particle forces. These motions lead to micro-convection leading to the enhancement of heat transfer. In nanoparticle–fluid mixtures, microscopic forces can be significant. Forces acting on nano-sized particles include the Van der Waals force, electrostatic force resulting from the electric double layer at the particle surface, the stochastic force due to Brownian motion and the hydrodynamic force. Motions of the particles and fluids are induced and affected by the collective

<table>
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<tr>
<th>Temperature (°C)</th>
<th>20 nm TEG+water-based</th>
<th>40 nm TEG+water-based</th>
<th>20 nm TEG-based</th>
<th>40 nm TEG-based</th>
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effect of these forces. Notice that the stochastic and electrostatic forces are significant only for small particles, whereas the Van der Waals force is high at small inter-particle distances. Therefore, there exists a correlation between the effective thermal conductivity and the particle size [52].

Comparison with thermal conductivity models

Some models are summarized in Table 3 for the prediction of effective thermal conductivity of solid–liquid mixtures. Comparison of these empirical correlations and experimental data are given in Figs. 12 and 13. The difference between Li & Peterson model and experimental data is because the model was obtained for 27-36 °C and very high concentrations (2-6 vol.%) contrary to this study [49, 30]. In fact, it is clear that the higher concentration of nanoparticles could lead to higher thermal conductivity values besides the fact that in their study, the base fluid was pure water which may result in the difference in Fig. 12.

As said, Fig. 13 illustrates that the measured data are approximately in good agreement with the other empirical models except Nan’s model. The main reason for the difference between Nan’s model and the outcomes of this study is related to the significant impact of CNT (used in experimental section of Nan’s study and their empirical model) to improve thermal conductivity. Moreover, this effect of CNTs on the thermal conductivity of nanofluids can be seen in Fig. 14. Furthermore, Nan’s model was modified for
thermal conductivity measurement of CNT-based nanocomposites (given in the remarks section of Table 3). For other empirical models, the slight difference may be due to the inherent difference between base fluids applied in previous studies and this study. As shown in the table, the base fluid applied in most models is water, with a completely different thermal conductivity behavior compared with TEG. Fig. 13 reveals that different thermal conductivities are obtained by the mentioned models at each condition, which can be attributed to the very complex behavior of nanofluids showing that no general equation is proposed yet for prediction of thermal conductivity in these solvents [56, 48].

Furthermore, Fig. 14 demonstrates the obtained thermal conductivity values vs. diverse nanoparticle concentrations for both different nanofluids in this study at 60 °C which compared to other experimental studies that utilized KD pro Decagon thermal analyzer at various temperatures. As can be seen, there is a similar trend with other outcomes from literature; however, the supreme influence of CNTs on the thermal conductivity of nanofluids was shown and compared to other types of nanoparticles.

CONCLUSIONS
Thermal conductivity of TEG-water nanofluids was measured and compared with base fluids without nanoparticles. It was found that CuO nanoparticles can increase the thermal conductivity of the base fluid considerably. Thermal conductivity of TEG-water nanofluid is enhanced vs. temperature. The largest thermal conductivity enhancement for two types of nanofluids were acquired at nanoparticle concentration of 0.9 wt.%. Indeed, it is clear that increasing the particle concentration which can also be translated as the reduction of particle-to-particle distance leads to improvement of thermal conductivity. Based on the results, the highest augmentation is ~13.5% for the 0.9 wt.% nanofluid with 20 nm nanoparticles at 60 °C. Therefore, in order to enhance the thermal property of dehydration desiccant and utilization of nanofluids in gas dehydration process, smaller particles should be utilized.

DISCLOSURE STATEMENT
All authors declare that they have no conflict of interest in the publication of this manuscript.

REFERENCES


