Synthesis and Characterization of Fe$_3$O$_4$ Nanoparticles for Nanofluids from Local Material through Carbothermal Reduction and Precipitation

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Abstract
Nanoparticles of Fe$_3$O$_4$ for heat transfer nanofluids have been synthesized using precipitation method by utilizing Fe$_3$O$_4$ nanoparticles extracted from local material of yarosite. The precipitation was done by utilizing Fe$_3$O$_4$ powder that made by reducing the Fe$_3$O$_4$ using graphite (carbothermal process). Nanofluids of water-Fe$_3$O$_4$ were prepared from the Fe$_3$O$_4$ nanoparticles. According to XRD data, it was known that the Fe$_3$O$_4$ nanoparticles crystalized in spinel cubic with crystallite size of 12 nm. TEM analyses showed that the particle size was about 16 nm. This data is in agreement with the XRD data. The Fe$_3$O$_4$ powder possesses large surface area of 181 m$^2$/gram. The water-Fe$_3$O$_4$ nanofluid with CA dispersant were prepared with Fe$_3$O$_4$ concentration 0.10-0.74g/100ml. The nanofluids were stable with zeta potential - 35 mV to -45 mV. Critical Heat Flux (CHF) of the water-Fe$_3$O$_4$ nanofluids was larger than that of water and increased as increasing of Fe$_3$O$_4$ nanoparticles concentration. The increase of CHF was 185% for the nanofluid with Fe$_3$O$_4$ concentration of 0.7385 g/100 ml.

Keywords: Nanofluids, Fe$_3$O$_4$, nanoparticles, local materials, heat transfer, carbothermic, precipitation, CHF.

INTRODUCTION
Efficiency of a heat transfer system can be increased by utilizing a coolant with better characteristic than base fluids such as water. Nanotechnology can be used to create a new coolant. Nanofluids as one of application of nanotechnology have great potential to be the new coolant. The nanoparticle is a base fluid, such as water, oil and ethylene glycol, dispersed with 1-100 nm nanoparticles forming a stable suspension [1-4]. Choi proposed term of nanofluid in 1995 [5]. Large surface-to-volume ratio of nanoparticles can lead to potential significant enhancement of thermal conductivity of fluids.

Among ceramic nanoparticles can be used to produce the nanofluids, the nanoparticles of Fe$_3$O$_4$ has been widely used to prepare nanofluids [6-12]. The Fe$_3$O$_4$ nanoparticles are generally used for producing biomedical nanofluids for some applications such as imaging, drug delivery and cancer therapy [6-12]. Study on the nanofluids of water-Fe$_3$O$_4$ for heat transfer application is relatively rare, although some were found [13-15].

In our previous study [13], nanofluids of water-Fe$_3$O$_4$ for heat transfer was studied utilizing Fe$_3$O$_4$ made of local material of yarosite. Synthesis of Fe$_3$O$_4$ with yarosite as raw material was carried out in order to increase the added value of the local material. Good thermal characteristics were shown by the nanofluids prepared using the Fe$_3$O$_4$ nanoparticles synthesized in the previous study [13], however, the synthesis of Fe$_3$O$_4$ using co-precipitation method in that study was less efficient. In this study, the synthesis of Fe$_3$O$_4$ was done by combination of carbothermal and precipitation methods. The synthesis of Fe$_3$O$_4$ nanoparticles in this study is simple and more efficient compared to the method in our previous study [13]. Water-Fe$_3$O$_4$ nanofluids were prepared utilizing the synthesized Fe$_3$O$_4$ nanoparticles. Discussion of the synthesis and characteristics of the Fe$_3$O$_4$ nanoparticles was carried out. The preparation and characteristics of the water-Fe$_3$O$_4$ nanofluids were also discussed.
METHODOLOGY

Synthesis of Fe₃O₄ nanoparticles

Main material of Fe₃O₄ nanoparticles was prepared using a method described in our previous study [13]. An amount of yarosite, a local mineral containing Fe₂O₃, was dissolved in HCl. Ammonia was added into the solution until pH larger than 7. Then, a precipitate was formed. Precipitate was separated by filtration, and washed using aquadest. After that, the precipitate was calcined at 700°C for 3 hours to form Fe₂O₃ nanoparticles. An amount of the Fe₂O₃ nanoparticles was mixed with graphite and pressed under low pressure. The pressed mixture was heated at 1000°C for 70 minutes (reduction process). The reduced Fe₂O₃ was dissolved in HCl. Ammonia was drop wise into the solution until black precipitate was formed (pH 9-10). The precipitate was washed using aquadest until pH about 7. The Fe₃O₄ nanoparticles were analyzed using X-ray diffraction (XRD) with step size 0.019°. The x-ray radiation was from a Cu Kα target with λ = 1.5406 Å. In order to know the particle size, the nanoparticles were also analyzed by means of a Transmission Electron Microscope (TEM) JEM-1400 from JEOL operating at accelerating voltage of 120 KV. Surface area of the nanoparticles was also measured using a surface area meter from Quantachrome. A visual picture of the nanoparticles was also taken by using a digital camera. Magnetic property of the Fe₃O₄ nanoparticles was measured using a Vibrating Sample Magnetometer (VSM).

Preparation of water-Fe₃O₄ nanofluids

An amount of Fe₃O₄ nanoparticles of 0.125, 0.25, 0.5, and 1g was suspended in 100 ml water (aquadest), and 20% of each weight of Fe₃O₄ citric acid (CA) as dispersant was added into the suspensions. pH of the suspension was controlled to be 7 by addition of NH₄OH. The nanofluid was ultrasonicated for 2 hours. After 3 days, precipitate formed at the bottom of bottle was taken. The rest is nanofluid part. The nanofluids were observed visually time to time. Visual pictures of the nanofluids were taken by using a digital camera. The zeta potential of the nanofluids was measured using zetasizer from Malvren. Thermal conductivity of the nanofluids was measured using a thermal conductivity meter of KD2 Pro. Critical Heat Flux (CHF) of Cu wires inside the same nanofluid was also measured at temperature of 98°C (water boiling condition) using a method described in reference [13,16, 17].

RESULTS AND DISCUSSION

Synthesis and Characterization of Fe₃O₄ nanoparticles

Fig. 1 is visual appearance of Fe₃O₄ nanoparticles synthesized in this study. The XRD pattern and TEM image of the nanoparticles are shown in Fig.2 and Fig.3, respectively.

As shown in Fig. 2, the peak intensities show that the powder possesses the characteristics of perfect crystal. The XRD pattern revealed well developed reflection of Fe₃O₄ nanoparticles with cubic structure, which is in agreement with JCPDS. No. 19-0629. No addition peaks from FeO that can be identified indicating a perfect reaction during carbothermal reduction utilizing graphite. Some strong Bragg reflections corresponding to the reflection of Fe₃O₄ nanoparticles are clearly seen. The XRD pattern of the Fe₃O₄ nanoparticles displays the peaks at 2θ=30.095°, 2θ=35.422°, 2θ=43.052°, 2θ=53.391°, 2θ=56.942°, and 2θ=62.515° which corresponds to the (220), (311), (400), (422), (511), and (440) planes, respectively.

The average crystallite size of the Fe₃O₄ nanoparticles was calculated from the XRD pattern using the Scherrer formula [14] as shown in Eq. 1.

\[ d_{hkl} = \frac{0.9 \lambda}{\beta \cos \theta} \]  

where \( d_{hkl} \) is the average crystallite size (nm), \( \theta \) is an angle of incidence, \( \lambda \) is the wave length of X-ray (\( \lambda = 0.15406 \) nm), and \( \beta \) is the full width at half maximum (FWHM). The calculated average crystallite size of the sample is 12 nm. This crystallite size is the same with that of the Fe₃O₄ nanoparticles in our previous study [13], and that of Chicea, et al of 11 nm [12], comparable to that of the sample of abareski et al (8.4-10.9 nm) [14], and smaller than that of the sample of Ansar et al of 22-28 nm [18], the sample of Arsalani et al of 19 nm [6], and the sample of Astuti et al of 30-104 nm [19]. This data indicates that the synthesis method used in this work is good enough and suitable for Fe₃O₄ nanoparticles production. The method is simpler and more efficient than that in our previous study [13].

Figure 1. Fe₃O₄ nanoparticles made by carbothermal and precipitation methods.
TEM image of Fig. 3 shows that the Fe₃O₄ nanoparticles are nearly spherical with average particle size of 14 nm (below 20 nm). This particle size is proportional to the crystallite size of 12 nm calculated using Debye Scherrer from the XRD data. Although, the particle size in this work is larger than that of Cheraghipour et al of 10 nm [20], the particle size of the synthesized Fe₃O₄ nanoparticles is still small enough with excellent surface area of 181 m²/g, so the nanoparticles are suitable for the nanofluids preparation. The surface area of 181 m²/g is larger than that of the Fe₃O₄ in our previous study that synthesized using coprecipitation method.

Fig. 4 displays the magnetization curve of the sample at room temperature. The sample exhibits superparamagnetic behavior with small coercivity and remanence. This is due to the fine crystallite sizes of Fe₃O₄ particles, which are in the nanoscale. The saturation magnetization (Ms) value is 81 emu/gram, which is lower than that of the bulk Fe₃O₄ (92 emu/g) [14]. However, this saturation magnetization is larger than that of Abareshi et al of 26-56 emu/g [14], Arsalan et al of 34-52 emu/g [6], Astuti et al of 11-45 emu/g [19], and Cheraghipour et al of 74 emu/g [20], and comparable to that of Fu et al 25-81 emu/g [21]. Considering the XRD pattern of the sample, the relatively large Ms value is caused by the good crystallinity of the sample. The well-crystallized particles have a thin non-magnetic surface layer and less superparamagnetic relaxation [14]. The magnetic property of materials is affected by the particle size. Although the nanofluid in this work is mainly for heat transfer application, but with relatively large saturation magnetization of 81 emu/g, the nanofluid prepared in this work is also suitable for bioapplication. According to Arsalani et al [6], the saturation magnetization for bioapplication is 7-22 emu/g.

Preparation and Characterization of Water-Fe₃O₄ nanofluids

After 3 days, the precipitate was separated from nanofluid part, and then stable nanofluids were formed with new concentration of Fe₃O₄ nanoparticles. Visual image of nanofluids is shown in Fig. 5. The prepared nanofluids of water-Fe₃O₄ are stable, and stay stable at least until 135 days (June 15, 2015). The stability is shown also by the zeta potential data in Fig. 6. As one can see that the zeta potential is larger than 25 mV or smaller than -25mV, means that the nanofluids are stable. This fact shows that the nanofluids are suitable for heat transfer nanofluids. Viscosity of the nanofluids can be seen in Fig. 7 after the concentration in Table 1 is converted to volume %. As shown in Fig. 7, the viscosity increases as the increase of Fe₃O₄ concentration. The increase of viscosity as the increase of concentration in this work is different with Einstein prediction [22] expressed in Eq. 2.

$$\mu_{nf} = \mu_{bf} (1 + 2.5\phi)$$

where $\phi$ is particle volume fraction, $\mu_{nf}$ is viscosity of nanofluid, and $\mu_{bf}$ is viscosity of base fluid. The increase of the viscosity as the increase of concentration of nanoparticles in the experiment is larger than the increase of the viscosity according to
Einstein prediction. This data shows that the viscosity of the nanofluids is influenced by many factors not only particles concentration as used for Einstein prediction. One important factor that makes a difference between the experimental data and Einstein prediction is the role of dispersant of citric acid. The dispersant has created strong interaction between nanoparticles.

Table 1. Concentration of nanofluids prepared in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0978g/100ml water</td>
</tr>
<tr>
<td>2</td>
<td>0.1985g/100ml water</td>
</tr>
<tr>
<td>3</td>
<td>0.3575g/100ml water</td>
</tr>
<tr>
<td>4</td>
<td>0.7385g/100ml water</td>
</tr>
</tbody>
</table>

The increase reaches 185% when the concentration of Fe₃O₄ is 0.7385 g/100 ml. The increase is comparable to that in our previous study [13]. The coating of heat transfer surface causes the increase of CHF by the nanoparticles. This coating then increases heat transfer process. This large increase of CHF shows that the nanofluids prepared in this work has potentiality to be applied for heat transfer nanofluid, as coolant for automotive or for emergency core cooling system (ECCS) and reactor vessel cooling system (RVCS) of nuclear reactor, and as fluid that used during machining and grinding.

Fig. 8 shows the increase of critical heat flux (CHF) as function of Fe₃O₄ concentration. The CHF of the water-Fe₃O₄ nanofluids is larger than that of water. So, the increase of CHF is defined as the difference between the CHF of the water-Fe₃O₄ nanofluids and the CHF of water divided by the CHF of water multiplied by 100%. It can be seen that the increase of CHF increases as the increase of Fe₃O₄ concentration.

CONCLUSIONS

Nanoparticles of Fe₃O₄ with crystallite size of 12 nm (TEM particle size of 14 nm) have been well synthesized from local material of yarosite using combination of carbothermal reduction and precipitation methods. Stable nanofluids of water-Fe₃O₄ have been prepared from the nanoparticles of Fe₃O₄ with zeta potential -35 to -45 mV. The CHF (Critical Heat Flux) of the nanofluids is larger that of water, and increases as the increase of concentration of Fe₃O₄ nanoparticles. The increase of CHF reaches
185% at Fe$_3$O$_4$ concentration of 0.7385 g/100 ml. This nanofluids prepared in this work is possible to be applied for heat transfer nanofluid, as coolant for automotive or for emergency core cooling system (ECCS) and reactor vessel cooling system (RVCS) of nuclear reactor, and for fluid that used during machining and grinding. The nanofluids may also be applied for bioapplication due to the large saturation magnetization.

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