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Nanofluids with Enhanced CHF Prepared from Solgel Synthesized Al_2O_3 Nanoparticles Utilizing Urea as Chelating Agent

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***Abstract*—In order to develop a new coolant for nuclear and non-nuclear applications, nanoparticles of Al_2O_3 for nanofluids have been successfully synthesized by solgel method utilizing $AlCl_3$ as precursor and urea as chelating agent. The mole ratio of the $AlCl_3$ and urea was 1:2. The solution was stirred to form a sol and then was heated at 150ºC until forming a gel. The gel was then calcined at 500ºC for 1 hour to get Al_2O_3 nanoparticles. Nanofluids of Al_2O_3 were prepared by dispersing the Al_2O_3 nanoparticles into water as base fluid. The synthesized Al_2O_3 nanoparticles crystallized in gamma phase with crystallite size of 3.4 nm as confirmed by the XRD analyses. Specific surface area of the nanoparticles was 251 m^2/g with d_{BET} of 6 nm. As confirmed by TEM analyses, the particle size of the nanoparticles was 35 nm. The nanofluid with concentration of 0.05 vol % and pH of 7.42 possessed zeta potential of 53 mV, indicating a stable suspension. This nanofluid had a CHF enhancement of 92% compared to water as base fluid.**

Keywords—Nanoparticles; Al_2O_3; solgel; urea; nanofluids; CHF

I. INTRODUCTION

It is currently known that various heat transfer systems such as automotive, nuclear reactors, and metal machining use water as its heat transfer fluid. Along with the development of the time the economic level and safety of these systems need to be increased. Various methods can theoretically be pursued such as increasing the number of fluid distribution pipes and increasing flow velocity, but these methods are not economical. The best way is to replace the water fluid with a new fluid that has better heat transfer characteristics. Based on nanotechnology, there is a candidate for new cooling fluid called nanofluid. The nanofluid is dispersion of nanoparticles with size of 1-100 nm into a fluid that forms a stable suspension. This fluid was first time introduced by Choi from MIT United States in 1995 [1].

Currently nanofluids have been studied throughout the world. Various nanoparticles have been synthesized for the nanofluids such as Al_2O_3 [2-5], ZrO_2 [6], ZnO [7], Fe_2O_3 [8,9], Fe_3O_4 [10], carbon nanotubes [11], and graphene [12]. Meanwhile some of the basic fluids used are water and ethylene glycol. Among the various nanoparticles already mentioned, Al_2O_3 is very attractive because it has good thermal conductivity and a small thermal neutron absorption coefficient that is very suitable for nuclear applications. Al_2O_3 nanofluid has been widely developed, but still has problems related to its stability. Especially for primary cooling system of a nuclear reactor, nanofluids must be stable without the addition of dispersants that usualy used as stabilizers. Nanofluids can theoretically be applied to non-nuclear purposes such as automotive, computers, and metal machining, and nuclear ones such as primary cooling system, Emergency Core Cooling Systems (ECCS) and Reactor Vessel Cooling Systems (RVCS). The nanofluid for the stated purpose must have good stability and large critical heat flux (CHF).

Based on the theory, nanofluid stability can be changed by adding acids or bases, and organic dispersants. But for applications in primary cooling system of nuclear reactors the addition of these substances is not permitted because the added substances will interact with high dose radiation and high temperature. For other purposes besides the primary cooling system of nuclear reactors, both nuclear and non-nuclear, the addition of acid base and organic dispersants can be tolerated. Nanofluids that are suitable for primary cooling system of the nuclear reactor can automatically be used for other applications either in nuclear reactors or other applications outside nuclear reactor. The nanofluid studied in this study is that without organic dispersants.

Preparation of a stable nanofluid without the addition of dispersants is very difficult because nanoparticles tend to settle over time. In a suspension, nanoparticles tend to precipitate or settle. A nanofluid is stable since the precipitation takes place over a long period of time. The preparation of a stable nanofluid without the addition of dispersants can be done through the nanoparticle synthesis process.

In our previous researchs, efforts to prepare the stable nanofluids through nanoparticle synthesis engineering have been carried out by synthesizing Al_2O_3 nanoparticles using the solgel method with citric acid as chelating agent [13], and sugar [14] as well as PEG 1000 [15] as capping agents. However, the results obtained were still not satisfactory because the prepared nanofluid was relatively less stable with zeta potential around -40 mV. Therefore, in this study an attempt was made to prepare a more stable Al_2O_3 nanofluid with a larger zeta potential through the synthesis of Al_2O_3 using solgel method utilizing urea as a chelating agent.

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II. Methodology

A. *Material synthesis and Characterization*

Powder of $AlCl_3$ was dissolved in the water inside a beaker glass. Then a quantity of urea was poured into the beaker glass containing $AlCl_3$ and stirred until it was completely soluble and forming a sol. The mol ratio of $AlCl_3$ and urea was 1:2. The sol was heated at 175°C for 17 hours to form gel. Next the gel was calcined at 500ºC for 1 hour. Visual appearance of the Al_2O_3 nanoparticles as calcination product is depicted in Fig. 1. The Al_2O_3 nanoparticles were analyzed by X-ray Diffraction (XRD) to determine the crystal structure and to estimate the crystallite size. The XRD pattern was recorded with 2θ in the range 10-80º with Cu-Kα: l = 1.5609 Ǻ. The surface characteristic of the Al_2O_3 nanoparticles was analyzed using a Fourier Transform Infrared spectrometer (FTIR), and specific surface area was measured using a surface area meter from Quantachrome.

Fig. 1. Visual appearance of Al_2O_3 nanoparticles synthesized using solgel method.

B. *Nanofluids preparation and Characterization*

An amount of 0.2g of the Al_2O_3 nanoparticles calcined at 500ºC for 1 hour was dispersed into 100 ml aquadest as base fluid. In order to obtain well dispersed nanofluids, the mixtures were ultrasonicated for 2 hours. pH of the nanofluid was measured using a Mettler Toledo pH meter. Conversion to vol % concentration was done by using equation (1).

$$\phi = \frac{m_p / \rho_p}{m_p / \rho_p + V_{BF}} x100\% \quad (1)$$

where, ϕ is the Al_2O_3 concentration in vol %, m_p is the mass of Al_2O_3 nanoparticles, ρ_p is the density of Al_2O_3, and V_{BF} is the volume of the base fluid.

A Zetasizer from Malvren was used to measure zeta potential of the nanofluids. Pictures of visual appearance of the nanofluids were taken by using a digital camera. Critical Heat Flux (CHF) of the nanofluids was measured using a method described in [2,13-15] utilizing Cu wire with diameter of 0.1 mm. CHF enhancement is calculated using equation (2).

$$CHFenhancement = \frac{CHF_{NF} - CHF_{BF}}{CHF_{BF}} x100\% \quad (2)$$

where CHF_{NF} is Critical Heat Flux of the nanofluids and CHF_{BF} is Critical Heat Flux of the base fluid (in this case water).

III. Results And Discussion

A. *XRD analyses of Al_2O_3 nanoparticles*

Fig. 2 shows the XRD pattern of the Al_2O_3 nanoparticles synthesized using self combustion method utilizing urea as fuel. The pattern was analyzed by comparing it to the XRD patterns from JCPDS. According to the analyses, it was known that the nanoparticles crystallized in theta phase of Al_2O_3 which is in accordance with the JCPDS standard No. 33-0018. Base on the XRD pattern of Fig. 3, a calculation was performed employing Debye Scherrer method [2,14] represented in Equation (3). From the calculation it was known that the average crystallite size is 3.4 nm.

$$D = \frac{0.9\lambda}{\beta.Cos\theta} \quad (3)$$

where, D is crystallite size of the nanoparticles, β is the full width at half maximum (FWHM) in rad, λ is the wavelength of X-rays (λ = 0.15406 nm), and θ is the Bragg's angle (an angle of incidence).

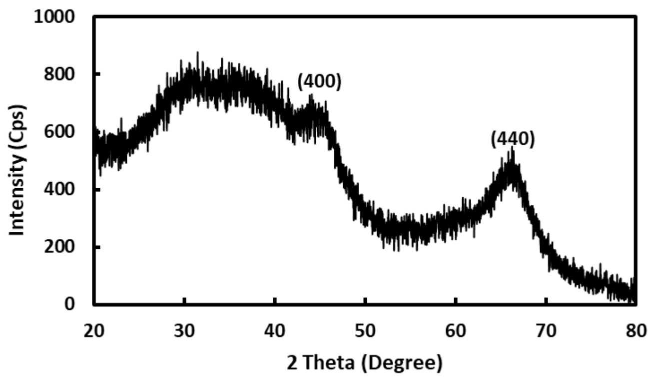

Fig. 2. XRD pattern of Al_2O_3 nanoparticles.

B. *Surface Area analyses and particle size*

Specific surface area of the nanoparticles was 251 m^2/g and by using equation (4), it was converted to particle size (d_{BET}) of 6 nm.

$$d_{BET} = \frac{6000}{S.\rho} \quad (4)$$

where d_{BET} is BET particle size (nm), S is specific surface area (m^2/g), and ρ is density of Alumina (g/cm^3).

C. *FTIR analyses of Al_2O_3 nanoparticles*

Fig. 3 depicts the FTIR spectra of Al_2O_3 nanoparticles synthesized in this work. The presence of functional group is usually identified at wave number of 1500-4000 cm^{-1}. The wave number from 600-1500 cm^{-1} is fingerprint region. The band at around 1638 cm^{-1} corresponds to the bending vibration of O–H, and the band around 3451 cm^{-1} is assigned to the stretching vibrations of surface adsorbed water and vibration bands of bonded hydroxyl groups [16]. This data shows the number of hydroxyl groups on the surface of γ-alumina nanoparticles. According to this data, a number of hydroxyl groups exist on their surfaces. According to Fig. 3, the stronger broadening bands from 400 to 1000 cm^{-1} for –Al–OH and –O–Al–O–Al– correspond to the characteristic vibration of Al_2O_3. The same characteristic was found in a work of Khazaei et al [17] and in our previous study [2,13-15].

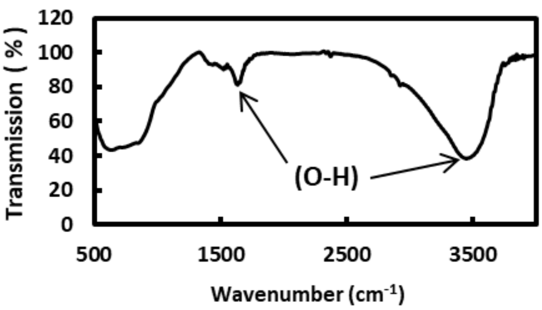

Fig. 3. The FTIR spectra of as-synthesized nanoparticles with calcination temperature of 500°C.

D. *Characterization of Al_2O_3 nanofluids*

Fig. 4 displays visual appearance of the nanofluids with Al_2O_3 concentration of 0.05 vol % with pH 7.42. Fig. 5 depicts the zeta potential of the nanofluid at different observation time. It is generally known that a suspension with zeta potential larger than 30 mV or smaller than -30mV is stable. The nanofluids in this work possess the zeta potential larger than 30 mV namely 53 mV (average) as shown in Fig. 5, indicating that the nanofluids are stable. At least until 19 days the nanofluid was very stable. Compared to the zeta potential of our nanofluids in our previous studies [2,13-15], the zeta potential in this work is larger, means that the nanofluid in this study is more stable than the nanofluids in previous studies [2,13-15]. The large the repulsion force on the nanoparticles, the large the zeta potential. As the consequence, the large the zeta potential is, the stable the nanofluids. The population of charges on the surface of the nanoparticles is influenced by the synthesis process of the Al_2O_3 nanoparticles. In this work, the charges formation was caused by the urea that used as the chelating agent during synthesis of the Al_2O_3 nanoparticles.

CHF enhancement of the nanofluid is 92 %. The Al_2O_3 nanoparticles are coated on the surface of Cu wire. The nanoparticles coating increases wettability of the Cu surface that causing the larger heat transfer from the wire to the nanofluid. The increase wettability delays the departure of water from the surface of the wire making the CHF increases. Compared to our previous study [2,13-15], the CHF enhancement of the nanofluids in this work is larger. This is due to larger zeta potential and smaller particle size. The particles size of the nanoparticles in this work is smaller than that in our previous study. Compared to some reported values of CHF enhancement [18], the CHF enhancement of the nanofluids in this study is comparable and large enough.

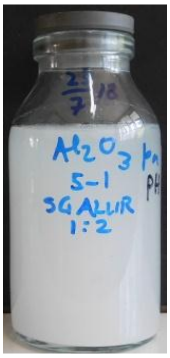

Fig. 4. Visual appearance of the nanofluid of Al_2O_3 with concentration of 0.05 vol % after preparation.

Fluid with large CHF was required for some applications such as RVCS and ECCS in Nuclear Reactor [19], metal machining [20], and quenching [21,22]. Benefit of the application of nanofluids in metal machining [Shokohii 20] covering drilling, turning, milling, and drilling was reported in a literature [20]. According to Shokoohi and Shekarian nanofluids can reduce cutting force, machining temperature, tool wear, and surface roughness in metal machining process [20]. The nanofluids in this work are potential to be applied in metal machining process. Bang and Kim reported [19] that their nanofluid with the cooling rate (230°C/s) that faster than pure water (218°C/s) may be applied for the RVCS and ECCS application. With enhanced CHF, the nanofluids prepared in this work are also possible to apply in RVCS and ECCS.

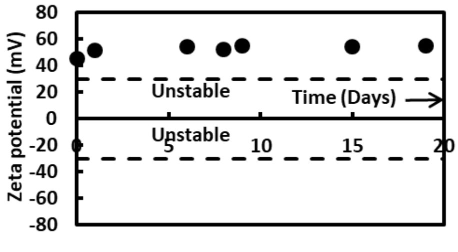

Fig. 5. Zeta potential of Al_2O_3 nanofluids at different observation times (Al_2O_3 concentrations is 0.05 vol %).

IV. Conclusion

Nanoparticles of gamma Al_2O_3 with crystallite size of 3.4 nm, d_{BET} of 6 nm have been well synthesized by using solgel method utilizing urea as chelating agent. Nanofluids prepared by utilizing these Al_2O_3 nanoparticles with calcination temp of 500°C possessed average zeta potential of 53 mV indicating stable suspensions. The CHF enhancement of the nanofluid was 92 %, compared to water as base fluid. With this characteristic, the nanofluids are potential for cooling fluids of metal machining, quenching, RVCS, and ECCS.

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