Self combustion synthesis of Al$_2$O$_3$ nanoparticles from bauxite utilizing sugar as fuel for nanofluids with enhanced CHF

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Abstract. Nanofluids have big potential to replace conventional coolant such as water. Nanoparticles of Al$_2$O$_3$ for nanofluids has been successfully synthesized using self combustion method using sugar as fuel. Al(OH)$_3$ was used as precursor. It was extracted from local bauxite. The combustion was performed at 450°C. The combusted material was calcined at 1200°C for 1 hour to get Al$_2$O$_3$ nanoparticles. The Al$_2$O$_3$ nanoparticles were dispersed into an amount of water as base fluid to form nanofluids. XRD analysis revealed that the Al$_2$O$_3$ nanoparticles crystallized in theta phase with crystallite size of 15.5 nm. According to TEM analyses, the particle size was 30 nm. The nanofluid with concentration of 0.025 vol % and pH 10 possessed zeta potential of -45 mV indicating a stable suspension. Compared to water as base fluid, the nanofluid prepared in this study had a CHF enhancement of 70% making the nanofluids are potential for cooling fluids of metal machining, quenching, Reactor Vessel Cooling System (RVCS), and Emergency Core Cooling System (ECCS).

1. Introduction
Various essential systems and equipment that possess heat transfer system have been applied for many years to accompany human life. Such systems and equipment include nuclear reactors, automotive, metal machining process, and quenching process. The cooling system is operated by utilizing a coolant or coolant fluid. Parts of a nuclear reactor that require a cooling fluid are primary cooling systems that keep the temperature of the reactor core, secondary cooling system, Emergency Core Cooling System (ECCS), and Reactor Vessel Cooling System (RVCS) [1,2]. Cooling fluid is also required for heat removal during metal machining process [3], for automotive heat management [4], and for rapid cooling of metal in metal industry [5, 6]. To improve the economic level and safety of the heat transfer system, conventional methods are not economical anymore so there is a need to choose a special way. One alternative special attempt is to improve the performance of a cooling fluid or to replace it with a new type of fluid. Based on nanotechnology, a new fluid known as nanofluid was first introduced by Choi [7]. Since its inception by Choi in 1995 [7], nanofluids were continues to be intensively studied around the world. Nanofluid is the mixture of nanoparticles with size of 1-100 nm and base fluid forming a stable suspension. Nanofluids consist of base fluids such as water, oil, ethylene glycol, and glycerol, and nanoparticles such as Al$_2$O$_3$ [8-11], Fe$_3$O$_4$ [12], Fe$_2$O$_3$ [13,14], ZrO$_2$ [15], ZnO [16], and SiO$_2$ [17]. Among the nanoparticles already mentioned, Al$_2$O$_3$ is very attractive and important because it has good thermal conductivity and small neutron absorption coefficient [18]. In addition, the raw material of Bauxite is available in abundance in Indonesia. Al$_2$O$_3$ can be synthesized by various methods such as solgel [19, 20], precipitation [18, 21], self combustion [22], hydrothermal[23], and spray pyrolysis [24].
A very important characteristic for nanofluid is its stability, and the stability of nanofluid is affected by the nanoparticles surface characteristics. Generally in most studies of nanofluids, material synthesis is more directed to obtaining very small particles (nanoparticles) and is not directed to adjust the surface characteristics of the nanoparticles. Nanofluid stabilization can be performed in various ways including providing surfactants, dispersants, acids, and bases. However, some applications do not allow adding dispersants or surfactants, and acids such as for primary cooling system of the Nuclear Reactor. It is therefore the best way is to synthesize the nanoparticles in the same time adjusting their characteristics to suit the nanofluid. In our previous study, we attempted to synthesize as well as adjust the surface characteristic of Al₂O₃ nanoparticles by synthesizing the Al₂O₃ nanoparticles using sol gel method utilizing chelating agent of citric acid[19]. However, the nanofluid stability in our previous study was still low. Therefore in this study we did synthesis of Al₂O₃ nanoparticles using self combustion method by employing sugar as capping agent as well as fuel. Sugar was used to improve the surface characteristic of the Al₂O₃ nanoparticles.

2. Experimental Methods

2.1 Material synthesis and Characterization

Extraction of Al(OH)₃ from local bauxite was done using a method described in [8, 9]. The Al(OH)₃ powder was put into a beaker glass containing water. An amount of marketed sugar was then poured into the beaker glass until completely dissolved. The mixture formed a sol. The ratio of Al(OH)₃ and sugar (contains most sucrose) was 1:1. The sol was heated at 150°C until forming a gel. The gel was self combusted at 450°C and heated at 600°C for 10 minutes. Visual appearance of the self combustion process is shown in Fig. 1. The self combusted material was calcined at 1200°C for 1 hour to get Al₂O₃ nanoparticles. Visual appearance of the Al₂O₃ nanoparticles can be seen in Fig. 2. Identification of the crystalline phase and estimation of the crystallite size were performed using an X-ray diffractometer (XRD). The angle of 2θ was recorded in the range 10-80° with Cu-Kα: λ = 1.5609 Å. The nanoparticles were also analyzed using Fourier Transform Infrared spectrometer (FTIR) to evaluate the surface characteristic of the nanoparticles, and Transmission Electron Microscope (TEM) to know the particle size.

2.2 Nanofluids preparation and Characterization

Al₂O₃ nanoparticles calcined at 1200°C for 1 hour of 0.05g were dispersed into 100 ml aquadest as base fluid. The mixture was then ultrasonicated for 2 hours to form nanofluids with good dispersion of nanoparticles. A Mettler Toledo pH meter was used to measure the pH of the nanofluids. Other nanofluids with different nanoparticles weight namely 0.1g and 0.4g were prepared with the same step. The pH was adjusted to be 10 by addition of NH₄OH.

The Al₂O₃ nanoparticles concentration in vol % was calculated using equation (1).

\[
\phi = \frac{m_p / \rho_p}{m_p / \rho_p + V_{BF}} \times 100\% 
\]
where, $\phi$ is the Al$_2$O$_3$ concentration in vol %, $m_p$ is the mass of Al$_2$O$_3$ nanoparticles, $\rho_p$ is the density of Al$_2$O$_3$, and $V_{BFV}$ is the volume of the base fluid.

A Zetasizer from Malvern was used to measure Zeta potential of the nanofluids. Meanwhile, a digital camera was used to take pictures of visual appearance of the nanofluids. The method in [8] was used to measure Critical Heat Flux (CHF) of the nanofluids utilizing Cu wire with diameter of 0.1 mm.

3. Results and Discussion

3.1 XRD analyses of Al$_2$O$_3$ nanoparticles

Fig. 3 (below) shows the XRD pattern of Al(OH)$_3$ (Gibbsite) derived from local bauxite. A modified Bayer process was used in the Al(OH)$_3$ extraction. The Al(OH)$_3$ powder was then utilized as precursor for synthesizing Al$_2$O$_3$ nanoparticles using self combustion method. The formation of Al(OH)$_3$ gibbsite showed that the heating of the precipitate during Bayer process was well done with suitable heating temperature (90-100°C). The heating at a relatively higher temperature tends to resulting in AlOOH (Boehmite).

![XRD pattern of Al(OH)$_3$ and Al$_2$O$_3$ nanoparticles](image)

The XRD pattern of the Al$_2$O$_3$ nanoparticles synthesized using self combustion method is also depicted in Fig. 3 (Upper). The pattern was analyzed by comparing to the XRD patterns from JCPDS. From the analyses it is known that the nanoparticles crystallized in theta phase Al$_2$O$_3$ which is in accordance with the JCPDS standard No. 33-0018. The average crystallite size is 15.5 nm as derived from a calculation using Debye Scherrer method [8,25] base on the XRD pattern of Fig. 3.

Although the nanoparticles of Al$_2$O$_3$ were calcined at a relatively high temperature of 1200°C, the particles size (15.5 nm) is still small enough. Other than that, some literatures show that at high temperature, the Al$_2$O$_3$ crystallizes in alpha phase [26, 27, 28], however, in this work the Al$_2$O$_3$ nanoparticles crystallize in theta phase. This fact shows the role of sugar in impeding the formation of alpha phase during calcination. It can be reported that Roque-Ruiz and Reyes-López synthesized alpha Al$_2$O$_3$ at 1050°C[27], the calcination temperature is far from 1200°C. Farahmandjou and Golabiyan synthesized alpha Al$_2$O$_3$ at 1000°C[28], the calcination temperature is also far from 1200°C, and Matori et al. synthesized alpha Al$_2$O$_3$ at 1200°C [26]. The liberation of sugar used for the synthesis that caped ion of Al and the formation of alpha Al$_2$O$_3$ need calcination temperature higher than 1200°C and calcination time longer than 1 hour during calcination.
Sugar in this work acts as a capping agent. The capping agent keeps the ions of Al separated each other and well dispersed, and then avoiding Al₂O₃ nanoparticles formed by the ions of the Al³⁺ to be large and keep small after the synthesis.

3.2. TEM data
The actual size of the particles was confirmed by using the transmission electron microscopic (TEM). Fig. 4 depicts the TEM image of the spherical shape Al₂O₃ nanoparticles with average particles size of 30 nm. The particles size is relatively small at a high calcination temperature compared to that derived by Farahmandjou and Golabiyan with calcination temperature of 600-1000°C [28]. Our nanoparticles are more spherical than theirs. They utilized Aluminum nitrate as the precursor and glycine as fuel. The formation of the smaller spherical nanoparticles in this work indicates the role of sugar as a capping agent other than as fuel. Compared to glycine, sugar is cheaper. So, sugar is more effective and economical with dual functions.

3.3. FTIR analyses of Al₂O₃ nanoparticles
The FTIR spectra of Al₂O₃ nanoparticles synthesized in this work is shown in Fig. 5. At wave number of 1500-4000 cm⁻¹, functional group is usually identified, whilst the fingerprint region is from 600-1500 cm⁻¹. The bending vibration of O–H is observed at around 1620 cm⁻¹, and the stretching vibrations of surface adsorbed water and vibration bands of bonded hydroxyl groups is identified at the band around 3500 cm⁻¹ [29]. This data confirms that the number of hydroxyl groups exist on the surface of γ-alumina nanoparticles. According to Fig. 5, the presence of the stronger broadening bands from 300 to 1000 cm⁻¹ for –Al–OH and –O–Al–O–Al– indicates the characteristic vibration of Al₂O₃. A work of Khazaei et al [30] and our previous study [8] show the same characteristic.

3.4. Characterization of Al₂O₃ nanofluids
Fig.6 depicts visual appearance of the nanofluids. Differences in white color levels reflect differences in nanofluid concentrations.

Table 1 depicts the zeta potential at different concentration of Al₂O₃ nanoparticles. A suspension having zeta potential larger than 30 mV or smaller than -30 mV is stable. As shown in Table 1, the nanofluids in this work with three different concentrations possess the zeta potential smaller than -30 mV indicating that the nanofluids are stable. Minus sign of zeta potential suggests that the nanofluids are basic and the charges distributed on the nanoparticles surface originating from OH⁻. The larger the minus charges on the surface is, the large the zeta potential is. As the consequence, when the zeta potential is larger, the nanofluids are more stable. The population of OH⁻ is affected by the synthesis process of the Al₂O₃ nanoparticles. In this study, the OH⁻ formation was caused by the sugar that used as the capping agent and the fuel during synthesis of the Al₂O₃ nanoparticles.
Fig. 6. Visual appearance of the nanofluids with different concentration of Al$_2$O$_3$ nanoparticles after preparation.

Table 1. Zeta potential and CHF of the nanofluids (pH 10).

| No. | Concentration of Al$_2$O$_3$ nanoparticles (% vol) | Zeta potential (mV) | CHF enhancement (%) |
|-----|---------------------------------------------------|---------------------|---------------------|
| 1   | 0.013                                              | -41                 | 56                  |
| 2   | 0.025                                              | -45                 | 70                  |
| 3   | 0.101                                              | -43                 | 68                  |

Table 1 also displays the CHF enhancement as function of Al$_2$O$_3$ nanoparticles concentration. The coating of Al$_2$O$_3$ nanoparticles on the surface of Cu wire increases wettability of the Cu surface. The increase wettability delays the departure of water from the surface of the wire making the CHF increases. Compared to our previous study [8], the CHF enhancement of the nanofluids in this work is slightly smaller. This is due to larger particle size and smaller zeta potential. The size of our nanoparticles in current work is larger than that in our previous study. However, compared to some reported study [2], the CHF enhancement of the nanofluids in this study is comparable and large enough.

Fluids with large CHF are required for some applications such as RVCS and ECCS in Nuclear Reactor [1], metal machining [3], and quenching [5, 6]. A literature shows the benefit of the application of nanofluids in metal machining [3]. Metal machining covers drilling, turning, milling, and drilling. According to Shokoohi [3], cutting force, machining temperature, tool wear, and surface roughness may be reduced by application of nanofluids. Considering the characteristic of our nanofluids, they may be applied in the metal machining process. Bang and Kim reported [1] 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.

4. Conclusion

A self combustion synthesis utilizing sugar as fuel and capping agent to produce Al$_2$O$_3$ nanoparticles has been well performed. The produced nanoparticles are spherical with theta phase. The Al$_2$O$_3$ nanoparticles possess crystallite size of 15.5 nm and particle size of 30 nm. This study showed that sugar is effective and economical as fuel and capping agent. Nanofluids prepared from the produced nanoparticles with pH of 10 were stable with zeta potential of -41 mV to -45 mV. Compared to base fluid (water), the CHF enhancement of the nanofluids were 56-70 %, making the nanofluids are potential for cooling fluids of metal machining, quenching, RVCS, and ECCS.

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6. References

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