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Synthesis and Stability of Cupric Oxide-based Nanofluid: A Novel Coolant for Efficient Cooling

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ABSTRACT

One of the bottle-necks in efficient energy recovery is attributed to the low thermal conductivity of common coolants. When the thermal conductivity of coolant is improved, the flow rate of coolant required and hence, energy required for pumping can be reduced. Nanofluids are novel class of fluids, prepared by dispersing nanoparticles in liquids like water, ethylene glycol-water mixture, oil etc. aimed at increasing the thermal conductivity of such coolants. In order to maximize the advantages of nanofluids, the particles chosen for dispersion must possess high thermal conductivity and maintain excellent colloidal stability. Cupric oxide has very high thermal conductivity (78 W mK^{-1}) compared to that of water (0.6 W mK^{-1}) and hence dispersion of cupric oxide in water will serve to conserve energy. We have developed cupric oxide-water nanofluids using a two-step method. Cupric oxide nanoparticles were synthesized by reduction of cupric acetate. Scanning electron micrographs revealed the presence of needle-shaped particles of 60 nm wide and 252 nm long. These particles were dispersed using ultrasonication and by the use of Cetyl Trimethyl Ammonium Bromide (CTAB) as dispersant. Stability was ascertained by visual observation of nanofluids stored undisturbed. The zeta potential was measured to be -30 mV. Electrostatic repulsion and steric repulsion are expected to be responsible for colloidal stability of CuO-water nanofluids. Particles with aspect ratio >1 provide higher enhancement in thermal conductivity as evident from Hamilton and Crosser model. Hence dispersion of these nanostructures in water will improve the thermal conductivity appreciably.

Key words: Nanofluids, dispersant, thermal conductivity, colloidal stability

INTRODUCTION

Heat dissipation is a major operation in many industries. To increase the heat dissipation, the normal approach is to increase the heat transfer area through the use of extended surfaces like fins or through the use of large number of tubes. This leads to increase in the size of heat exchanger. An alternate way to improve the heat dissipation is through the use of coolants with high thermal conductivity. When solid particles with higher thermal conductivity are dispersed in a liquid, the thermal conductivity of the resultant mixture increases (Wang and Mujumdar, 2007). Nanofluids, a name coined by Choi, are new class of fluids that are engineered by dispersing nanoparticles in

the range of (1-100 nm) in liquids like water, ethylene glycol-water mixture, oil etc. aimed at increasing the thermal conductivity of such coolants (Choi, 1995). Nanofluids possess superior thermal properties (high thermal conductivity) compared to traditional coolants. The smaller particle size, coupled with large surface-volume ratio increases the stability of the suspensions, apart from improving the heat transfer capabilities significantly (Eastman, 2005). The role of particle size and surface area on heat transfer between fluid and particle, as in the cases of thermal management applications involving solids, is well understood (Rajan *et al.*, 2006-2008).

Oxides of copper have also been studied owing to their high thermal conductivity compared to that of other metal oxides (Nasibulin *et al.*, 2001; Chang *et al.*, 2000). Cupric oxide nanofluids were prepared first by Nasibulin *et al.* (2001) where the precursor being copper (II) acetylacetonate was thermally decomposed at a higher temperature of 705°C resulting in a mixture of copper and cupric oxide nanoparticles. Since then, many methods have been used to synthesize cupric oxide nanoparticles and prepare nanofluids using them. Methods for the synthesis of CuO nanoparticles include thermal decomposition of copper oxalate (Zhang *et al.*, 2008), plasma decomposition of cupric hydroxide (Li *et al.*, 2009), microwave irradiation (Lanje *et al.*, 2010), sol-gel method (Topnani *et al.*, 2009), wet chemical reduction methods (Manna, 2009), sonochemical reduction method (Saez and Mason, 2009) and other pyrolysis methods (Bisht *et al.*, 2010). Here we report the synthesis of needle-shaped CuO particles by chemical reduction of copper acetate using sodium hydroxide. The effect of reaction time on morphology is also reported.

Viscosity and thermal conductivity data are important to predict the flow and heat transfer in any thermal management application employing convective heat transfer. The investigations on viscosity of nanofluids are relatively less compared to investigations on thermal conductivity of nanofluids (Wu *et al.*, 2009). Viscosity describes the internal resistance of a fluid to flow and it is an important property for all thermal applications involving fluids (Kwak and Kim, 2005). The pumping power is related with the viscosity of a fluid. In laminar flow, the pressure drop is directly proportional to the viscosity (McCabe *et al.*, 1993). Furthermore, convective heat transfer coefficient is influenced by viscosity (Xinfang *et al.*, 2000). Hence, viscosity along with thermal conductivity plays a vital role in influencing the performance of coolants removing heat through convective heat transfer.

The study of rheology of nanofluids can provide useful information on the microstructure, extent of aggregation both under static (low-shear) and dynamic (high-shear) conditions (Kwak and Kim, 2005).

During the preparation of nanofluids, nanoparticles tend to agglomerate under the action of Van der Waals forces, leading to the formation of larger clusters that settle rapidly. To overcome Van der Waals forces, the particle surfaces must be encapsulated by dispersant those induce steric repulsion. Alternatively, adjustment of dispersion pH to maintain high charge density on particle surface and hence higher absolute zeta potential can produce electrostatic repulsion to oppose Van der Waals force (Liu and Liao, 2008).

The use of surfactants like SDS, SDBS, Tiron, Oleic acid, Cetyl Trimethyl Ammonium Bromide (CTAB) for the preparation of nanofluids have been reported (Qiang *et al.*, 2007; Liu and Liao, 2008; Guedes *et al.*, 2009; Xuan and Li, 2000). We have dispersed CuO nanoparticles in water

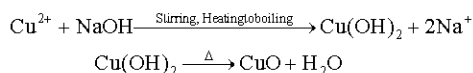
using Cetyl Trimethyl Ammonium Bromide (CTAB), a cationic surfactant and report viscosity for nanofluids prepared using CuO obtained at 2 different reaction times.

MATERIALS AND METHODS

Materials: All chemicals used in the experiment are analytical grade. Copper acetate monohydrate, Cetyl Trimethyl Ammonium Bromide (CTAB) and glacial acetic acid were purchased from Merck, India. Sodium hydroxide was purchased from Loba Chemie, India. Deionized water was used throughout the experiment.

Methods

Synthesis of CuO nanoparticles: CuO nanoparticles were synthesized by wet chemical reduction method using various available protocols of Zhu *et al.* (2011). To 0.2 M copper acetate solution, glacial acetic acid was added at acetic acid: copper acetate solution volumetric ratio of 1:300 and heated to boiling under continuous stirring. The 8 M sodium hydroxide solution was added to the boiling solution till the color of the solution turned from blue to black. The black suspension formed was heated to boiling under stirring for 2 h (Zhu *et al.*, 2011) and 24 h (Lanje *et al.*, 2010). The mixture was cooled to room temperature and filtered. The precipitate was washed twice with distilled water to remove the unreacted precursors and was dried in air for 24 h. The sequence of reactions that occur during the formation of CuO are as follows:



Preparation of nanofluids: Preparation of stable nanofluids is the first key step towards using them for heat transfer applications. The nanofluids are generally synthesized by two methods: single step method and two step method. In one step method, nanoparticles are synthesized and directly dispersed in base fluid, whereas in two step method, nanoparticles synthesis and their dispersion in a base fluid occur in two sequential steps (Chopkar *et al.*, 2006, 2007; Lee *et al.*, 1999). The nanoparticles are dispersed in base fluids by altering the pH (electrostatic stabilization), or by adding chemical activators or surfactants (steric stabilization), or by ultrasonication.

In this study, CuO-water nanofluids were prepared by two-step method with the aid of ultrasonication and steric stabilization. Nanofluids of various concentrations (0.2, 0.3, 0.4, 0.5, 1, 2 wt. %) were prepared by weighing CuO powders and dispersing in deionized water. Cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant was used as the dispersant to enhance the stability of CuO nanofluids at CuO:CTAB ratio of 1:0.2. The dispersions were homogenized for 15 min using high shear homogenizer (IKA® T25, Ultra-Turrax®, Germany). The homogenized dispersion was ultra sonicated (Vibra-cell™, Sonics, USA) for three hours to break down the agglomerates. Nanofluids were formulated with CuO powders obtained at two different reaction times of 2 and 24 h, respectively.

Characterization techniques

Scanning electron microscopy: The surface morphology of the nanoparticles was observed with Cold Field Emission Scanning Electron Microscope (JSM, 6701F, JEOL, Japan). CuO powders

obtained at 2 different reaction times were placed on the stub and sputter coated with platinum and loaded in to the specimen chamber. The samples were imaged at an accelerating voltage of 3 KV and at a working distance of 5.4 mm. The images were observed at magnifications of 10000 and 50000.

Spectroscopy: Absorption spectra of CuO-water nanofluids with CuO powder obtained at 2 different reaction times were obtained using UV-Visible spectrophotometer (Lambda 25, Perkin Elmer, Germany). The wavelength range used for scanning the samples was 200-800 nm. FT-IR spectra were recorded using Spectrum100, Perkin Elmer, USA for CTAB, CuO powder obtained at 2 different reaction times with and without CTAB to study the interactions between CTAB and CuO nanofluids. The wavenumber range used for recording the spectra was 400-4000 cm^{-1} .

X-ray diffraction analysis: The crystallinity of CuO powders obtained at 2 different reaction times were analyzed using X-ray diffraction analysis (X'PERT PRO, PANalytical, Netherlands). Cu $K\alpha$ radiation was used for recording the spectra. The samples were scanned at 2θ values from 10 to 79.9°.

Colloidal stability: The dispersion stability of CuO-water nanofluids was determined by measuring Zeta potential using a Zetasizer (Nano-ZS, Malvern Instruments, USA). CuO-water nanofluids formulated with CuO powder obtained at 2 different reaction times were diluted and the zeta potential was measured using a clear disposable cuvette.

Viscosity: Viscosity of nanofluids was measured using rotating cylinder viscometer (LV DV II+Pro, Brookfield Engineering, USA). The viscosity of the nanofluids was measured using S00 spindle using a Ultra-low (UL) adapter. Effect of temperature on the viscosities of the CuO-water nanofluids was studied at a temperature range of 25-60°C.

RESULTS

Characterization of nanoparticles

Morphology: Figure 1 shows the scanning electron micrographs of Cupric Oxide nanopowders prepared at two different reaction times of 2 h and 24 h (Fig. 1b, d) at magnifications of 10,000 and 50,000, respectively.

It may be observed from the low magnification (Fig. 1a) micrographs that the powders obtained after 2 h reaction time show predominantly sheet-like morphology along with the presence of some aggregates. The higher magnification micrograph (Fig. 1c) shows polydispersity in size, shape and orientation.

Scanning electron micrographs of cupric oxide nanopowder obtained from 24 h reaction time has uniform morphology (Fig. 1b) and well developed high aspect ratio structures predominantly with the width ranging from 20 to 30 nm and length above than 200 nm (Fig. 1d).

Spectroscopic analysis: The absorption spectra of synthesized CuO powders at reaction times of 2 and 24 h are depicted in Fig. 2, showing absorption band in UV region with λ_{max} around 280 nm for both the powders.

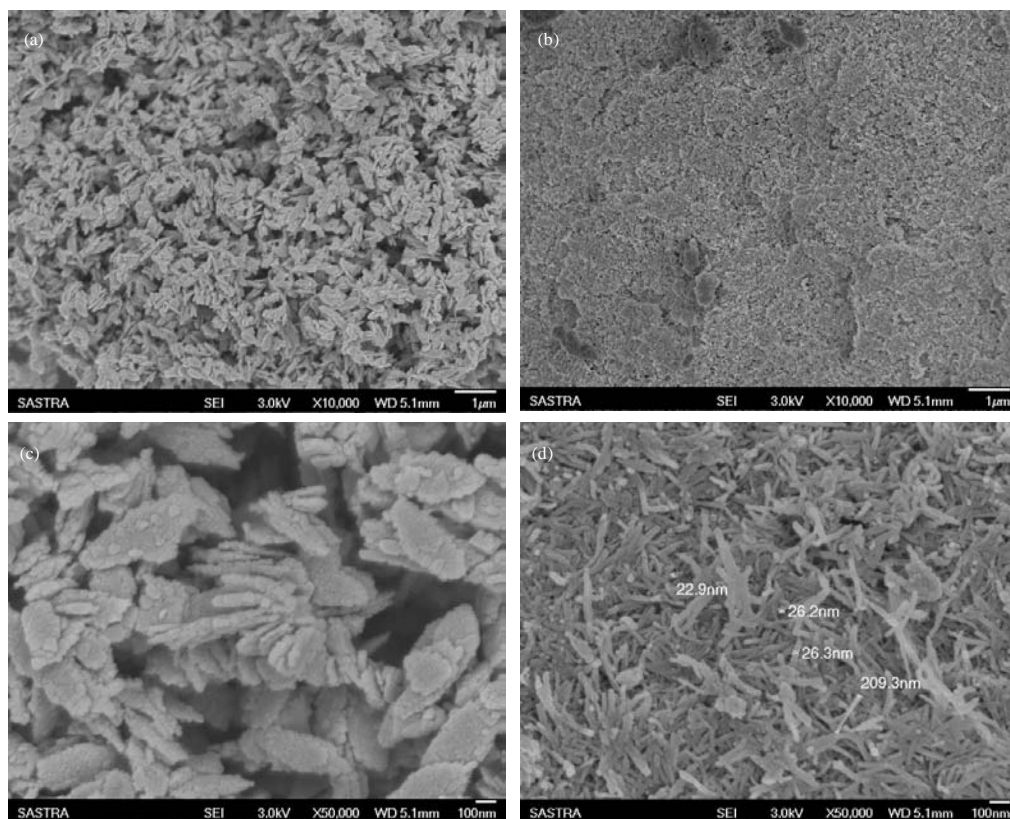


Fig. 1(a-d): Scanning electron micrographs of cupric oxide synthesized with reaction times of, (a) 2 h taken at a magnification of 10,000X, (b) 24 h taken at a magnification of 10,000X, (c) 2 h taken at a magnification of 50,000X and (d) 24 h taken at a magnification of 50,000X

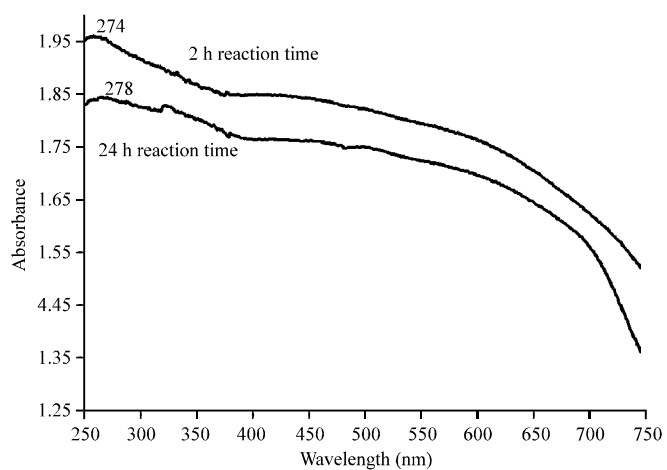


Fig. 2: UV-Visible absorption spectra of as-synthesized CuO nanoparticles of different reaction times

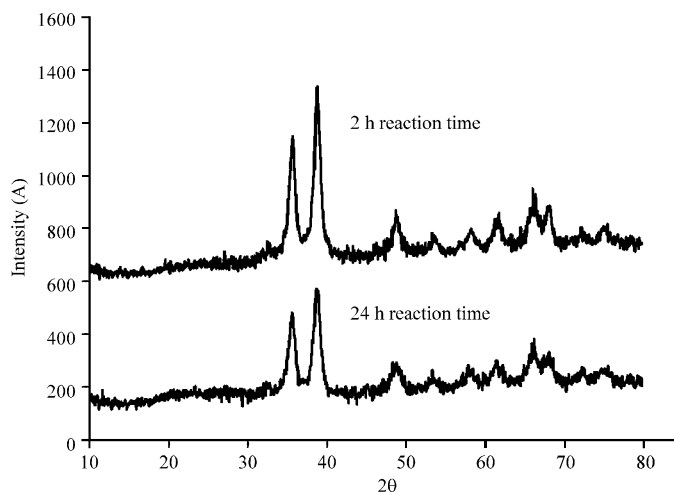


Fig. 3: XRD spectra of CuO powders synthesized with different reaction times

Crystallinity: The XRD spectra obtained for as-synthesized CuO powders of different reaction time of 2 and 24 h, respectively is shown in Fig. 3. The 2θ values corresponding to the most intense peak for powders obtained at reaction times of 2 and 24 h were found to be 38.84° and 38.83° , respectively.

Characterization of nanofluids

Fourier transform-infra red spectroscopy: Fourier transform Infrared spectroscopy is a valuable tool to understand the interaction between organic moieties and metal oxides. It may be recalled that CTAB has been utilized as dispersant in the present work. The FT-IR spectra of CTAB, CuO nanofluids and CuO dispersions without CTAB are shown in Fig. 4.

The peaks occurring at 606 , 503 and 437 cm^{-1} corresponds to the vibration of CuO band (Muhamad *et al.*, 2007). The nanofluids with CTAB have similar peaks as in peaks of CTAB's spectra in region $1000\text{-}4000\text{ cm}^{-1}$.

Viscosity: Figure 5a and b show the influence of temperature on viscosity of 0.5 and 1 wt. % CuO-water nanofluids respectively. It may be observed from Fig. 5a that the viscosity of nanofluids prepared with CuO powder synthesized with 2 h reaction time are lower than those obtained with CuO powder synthesized with 24 h reaction time. This pattern is observed till 40°C , after which the pattern is reversed.

However, for 1 wt. % CuO-water nanofluids, the viscosity of nanofluids prepared with CuO powder synthesized with 24 h reaction time was found to be lesser than that of nanofluids prepared with CuO powder synthesized with 2 h reaction time. This observation is different from those for 0.5 wt. % nanofluids.

Colloidal stability: The zeta potential values of cupric oxide nanofluids formulated using CuO nanoparticles synthesized with different reaction times (2 and 24 h) and stabilized with Cetyl Trimethyl Ammonium Bromide (CTAB) as dispersant are shown in Table 1.

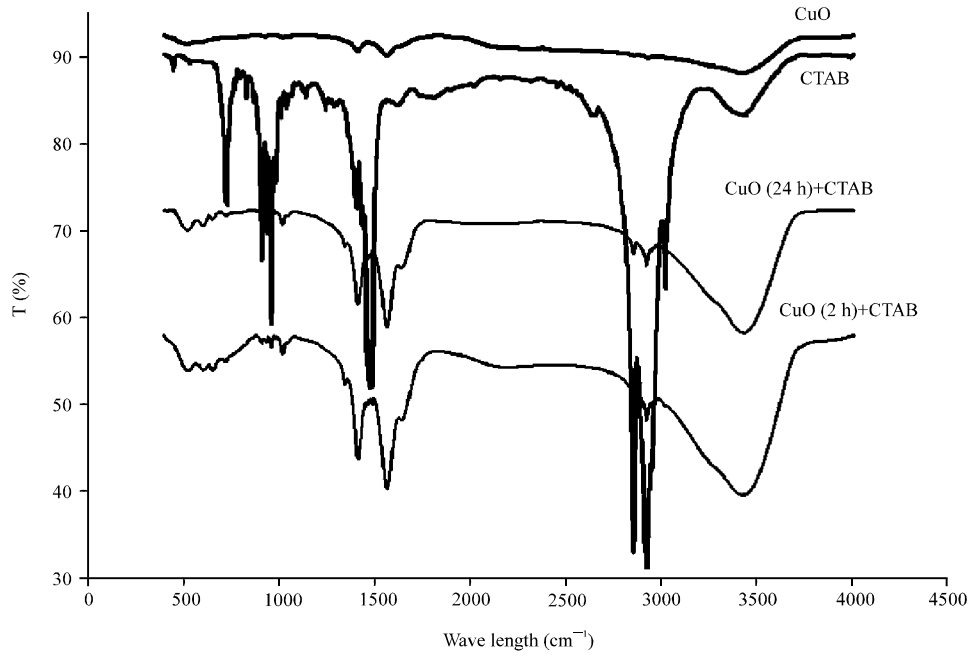


Fig. 4: Fourier Transform-Infrared Spectra of Cupric oxide nanofluid, Cupric oxide nanofluid stabilized with CTAB, CTAB of (a): 2 h cupric oxide nanoparticles, (b): 24 h cupric oxide nanoparticles

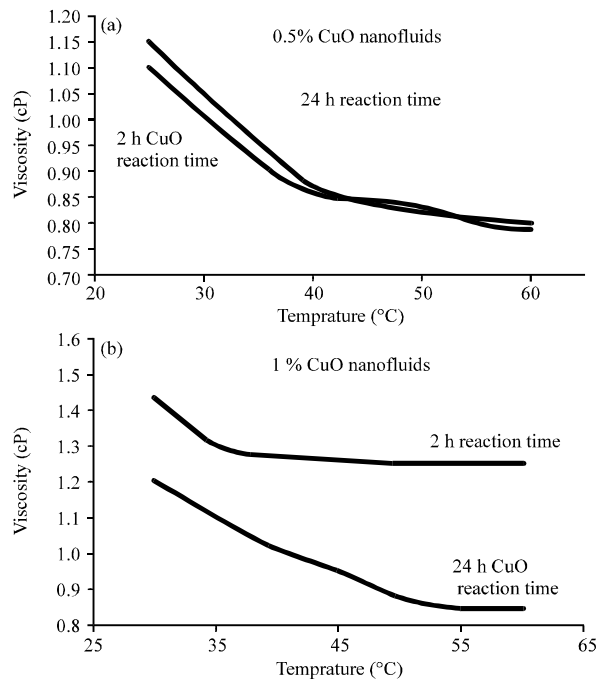


Fig. 5(a-b): Line graphs of (a): 0.5% CuO nanofluids' viscosity stabilized with CTAB versus temperature, (b): 1% CuO nanofluids' viscosity versus temperature

Table 1: Colloidal stability of cupric oxide of different reaction times stabilized by CTAB

Nature of sample	Cupric oxide (2 h) + CTAB	Cupric oxide (24 h)+CTAB
Zeta potential	28.03	25.23

DISCUSSION

The scanning electron micrographs (Fig. 1a-d) indicate that there is a strong influence of reaction time on the morphology of the powders obtained. At this stage, the mechanism of this influence is unclear, though we postulate that at lower reaction times, the sheet-like formation is characteristic of meta-stable structure, one of several of these types that can form before the nanostructures reach their stable final shape determined by the solution thermodynamics.

The UV-Visible spectra reveal the presence of CuO with characteristic λ_{\max} around 280 nm (Topnani *et al.*, 2009).

The peaks obtained in X-ray diffraction pattern can be indexed to that of monoclinic CuO (Zhu *et al.*, 2011). This confirms that the powder obtained at both the reaction times is CuO and are predominantly crystalline.

The peaks representing the vibration of Cu-O bond in FTIR spectra (Fig. 4) confirm the presence of CuO in both the as-synthesized particles and in the nanofluid (Swarnkar *et al.*, 2009). The absence of shift in the absorption bands between CTAB and nanofluids with CTAB indicate that the interaction between CuO and CTAB is physical.

The common observation among Fig. 5a and b is that nanofluids' viscosity decreases with increase in temperature for both 0.5 and 1 wt. % concentrations of CuO nanofluids and for both 2 and 24 h reaction time. This behavior is similar to that of liquids like water. Hence, the behavior of nanofluids will be similar to that of water when subjected to a temperature change.

The difference in trend between Fig. 5a and b testify the fact that nanofluids with irregular morphology are prone to easy aggregation compared to those with regular shaped particles. The attraction between nanoparticles leading to agglomerates increase with temperature and particle concentration (due to proximity) and hence, 1 wt. % nanofluids formulated with 2 h reaction time CuO are more viscous than those of 24 h reaction time, as obtained from Fig. 5b.

The zeta potential value indicated that the nanofluids prepared from CuO powder with 2 and 24 h reaction times exhibit moderate stability (zeta potential >25 mV).

CONCLUSION

CuO nanoparticles were synthesized by a wet chemical reduction method using copper acetate monohydrate as precursor. The synthesized CuO nanoparticles were found to have higher aspect ratios when reaction was allowed to occur for a period of 24 h.

CuO nanofluids formulated using CuO powder has been stabilized by using CTAB as dispersant. The colloidal stability of nanofluids was ascertained from zeta potential measurements. Higher viscosity measurement observed with nanofluids prepared using 2 h reaction time is attributed to agglomeration with size and shape heterogeneity.

Hence, from the study of rheology of these nanofluids, CuO nanoparticles prepared with higher reaction time is more suitable for engineering applications involving fluid flow and convective heat transfer.

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