Experimental investigation of stability and thermal properties of nanocellulose-water nanofluid

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Abstract. Nanocellulose defines as cellulosic materials in the nanometer range with at least one dimension. Nanocellulose is classified into three classes which are bacterial nanocellulose (BNC), cellulose nanofibrils (CNF), and cellulose nanocrystalline (CNC). Nanofluids had been widely been used in heat transfer applications because nanofluids are proven to have better thermal conductivity and enhance heat transfer performance compared with base fluid. However, liquid with suspended particles tends to destabilize, and sediments. Therefore, this study will uncover the effect of surfactant on the nanocellulose and its thermophysical properties. CNC with 0.1vol%, 0.5vol%, 0.9vol%, and 1.3vol% and Triton X-100 were used in this experiment. From the sedimentation observation after two weeks, there were no obvious agglomeration and sedimentation of CNC in the samples with surfactant compare with no surfactant. Furthermore, UV–vis spectroscopy analysis showed that samples with Triton X-100 have lower absorbance drop compare with no surfactant. This was due to the steric stabilization achieve for samples using Triton X-100. For thermal conductivity analysis, The highest reading of thermal conductivity was 1.224W/m.K for 0.5vol% at 40°C. Furthermore, the effective thermal conductivity achieves for 0.5vol% at 40°C was 1.301 compared with distilled water.

1. Introduction
Nanofluid is the dispersion of nano-sized particles (at least one dimension below 100nm) in a base-fluid i.e. water, alcohol, oil, refrigerant, etc. Some nanoparticle materials had been widely used are Nanoparticle materials consist of metal oxides such as alumina and silica, oxide ceramics (Al2O3, CuO); metal (Ag, Au, Cu, Fe); and single-, double-, or multi-walled carbon nanotubes (SWCNT, DWCNT, MWCNT). Nanofluids has widely been used in heat transfer applications because nanofluids are proven to have better thermal conductivity and enhance heat transfer performance compared with base fluid. Harun et al. [1] carried out an experimental investigation on the heat transfer performance of the loop heat pipe with nanofluids. The nanofluid used were diamond, Al2O3, and SiO2 for 0.5wt%, 1wt%, and 3wt%. Most of the nanofluids have thermal enhance compare to water and the highest was diamond at 3wt% which was 6.48%. Ali et al. [2] had done an experimental investigation of convective heat transfer augmentation for car radiators using ZnO–water nanofluids. Different volumetric concentrations had been used which were 0.01%, 0.08%, 0.2%, and 0.3%. The results showed heat transfer enhancement up to 46% was achieved by comparing it with pure water. There were other review papers on heat transfer application using nanofluids such as engine cooling system [3], heat exchanger [4], refrigerator [5], solar water heating [6], and electronic cooling [7].

To perform better in heat transfer applications, nanofluid need to have good stability where the nanoparticles suspended in the base-fluid, should not form large agglomeration leading to sedimentation.
of nanoparticle from the base-fluid [8, 9]. However, liquid with suspended particles tends to destabilize, and sediments due to various forces such as Van der Waal attractive force, gravitational force, buoyancy force, and electrostatic repulsive force [10]. Furthermore, according to Derjaguin Landau Vewey and Overbeek (DLVO) theory when Van der Waal's attractive potential dominates over electrostatic repulsive potential, particles tend to agglomerate and eventually lead to sedimentation [11]. There are two techniques to increase the stability of nanofluids which are mechanical and chemical. Most of the researchers used the ultrasonication method, using surfactant, and pH adjustment. After the stability analysis has been done, thermophysical properties can be analyzed properly.

Nanocellulose is defined as a cellulosic material in the nanometer range with at least one dimension. Klemm et al [12] classified nanocellulose into three classes which are bacterial nanocellulose (BNC), cellulose nanofibrils (CNF), and cellulose nanocrystalline (CNC). Due to rapid development in the sustainable field [13-15], nanocellulose is proposed in heat transfer applications as nanofluid. Harun et al [16] had a review of several applications of nanocellulose in the heat transfer application such as car radiator, cutting tools coolant, and pool boiling. Therefore, nanocellulose is one of the best candidates as one of the nanofluid’s materials that have green and environmentally friendly properties. Despite those studies, there is no study on the effect of surfactant with nanocellulose in preparing nanofluid. Therefore, this study will uncover the effect of surfactant on the nanocellulose and its thermophysical properties.

2. Methodology

2.1. Preparation of nanofluid

Nanofluid used in this experiment in CNC dispersed in distilled water for 0.1 vol%, 0.5 vol%, 0.9 vol%, and 1.3 vol% with and without Triton X-100 as the surfactant. CNC used was purchased from Blue Goose Biorefineries Inc which has 7.4% weight/weight suspension. The CNC has an average crystal diameter of 9-14nm, an average crystal length of 100-150nm, a hydrodynamic diameter of 150nm, and a crystallinity index of 80%.

The nanofluid was prepared using a two-step method process as shown in equation (1). The dilution method was used as shown in equation (2), to reduce the concentration of the CNC to the required volume concentration. After the ΔV amount of water was added in a beaker contain CNC, a magnetic stirrer was used to stir the mixture for 10 minutes at a speed of 400RPM or higher depending on the viscosity of the mixture. For the mixture with the surfactant, distilled water and surfactant were stir at a magnetic stirrer with 1:10 from the volume of CNC for five minutes to make sure that the surfactant was dissolved properly before adding the CNC. After that, add the required amount of CNC, V₁, and continue with another ten minutes of stirring using a magnetic stirrer. After that, the mixture was then sonicated using a probe sonicator (FS-1200 N, frequency: 20 kHz, power output: 1200 W, 18mm probe) for 15 minutes following by an ultrasonic bath (Elmasonic S100H) for 2 hours. During the whole sonication process, the sample temperature was maintained under 40 °C to prevent overheat and cause evaporation.

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\phi = \frac{\omega \rho b f}{(1 - \frac{\omega}{100}) \rho_{np} + \frac{\omega}{100} \rho b f}
\]

\[
\Delta V = (V_2 - V_1) = V_1 \left(\frac{\omega_1}{\omega_2} - 1\right)
\]
2.2. Evaluation of stability
The effect of adding a surfactant was studied on the stability of the CNC-water mixture. Non-ionic surfactant, Triton X-100 was used as a surfactant as it was the most suitable surfactant for non-metallic material such as nanocellulose. Steric stabilization cannot be quantified using zeta potential measurement since polymer attachment to the nanoparticle surface does not change the surface potential [10]. Therefore, a visual sedimentation method was used to observe the forming of agglomeration and sediment in the mixture. The observation was conducted for 2 weeks without moving or shaking the samples prepared. This method was the simplest method to assess the stability of a nanofluid over time. However, it lacks quantitative results to analyze the stability of the nanofluid. Therefore, the stability of nanofluids was further determined by using an ultraviolet-visible (UV-vis) spectrophotometer (Perkin Elmer Lambda 750). The absorbance drop of the nanofluid will determine the rate of sedimentation of nanofluid in terms of relative concentration (C/C₀).
2.3. Measurement of thermophysical properties

The thermal conductivity of CNC-water was measured using KD2 Pro, which was a transient hot-wire method. In this study, a KS1 sensor was used and it had an uncertainty of ±5.0% as it was the most suitable sensor for liquid analysis. As for equipment validation, the KS1 sensor had been tested with the glycerin sample at 20°C provided by the supplier and the result was accurate. The temperature involved was between 30°C to 50°C because the higher temperature the higher the error as the viscosity of the samples was very low. Lower viscosity samples increase the sensitivity of thermal conductivity reading due to the effect of convective heat transfer. Therefore, this experiment was set up using a water bath. The sample test tube was put in a water bath to make sure the temperature was in an equilibrium state. A total of 10 readings with an interval of 15 minutes were taken for each sample. An average value of thermal conductivity will be recorded for each sample.

3. Results and discussion

3.1. Characterization

3.1.1. Sedimentation observation

At first, the mixture of CNC-water was a bit cloudy. However, after the sonication using an ultrasonic probe and ultrasonic bath, the mixture became clear and transparent. This was because the particles of CNC have been dispersed more compared before sonication. Therefore, the mixture becomes clearer after the sonication. The prepared CNC-water samples were observed for 2 weeks without moving or shaking the samples.

The results of the sediment observation are shown in figure 5 and figure 6. After the preparation of the samples, both with and without surfactant has a clear and transparent solution. After two weeks, there was a formation of agglomeration of CNC in the CNC-water samples. Some of the agglomerations were floating in the solution due to the density of CNC and distilled water does not differ much. While some of the agglomerations sediment at the bottom of the tube due to the gravitational force. However, samples with Triton X-100 does not have obvious agglomeration and sedimentation after two weeks. This was because steric stabilization was achieved due to the presence of Triton X-100 as a non-ionic surfactant. When polymeric chains get absorbed on the nanoparticle surface, free movement of the nanoparticle in base-fluid is restricted and this acts as a steric diffusion barrier to prevent nanoparticle agglomeration [10].
3.1.2. **UV–vis spectroscopy analysis**

UV-vis spectroscopy method analysis was used to prove the nanofluid was scientifically stable. At first, the results show that the peak absorbance for all concentrations was between 260-268nm. One peak was chosen for each concentration to study the absorbance drop for four days. The list of peaks chosen for each concentration is shown in table 1.

| Sample                     | Peak(nm) |
|----------------------------|----------|
| CNC-water 0.1vol%          | 260.41   |
| CNC-water 0.5vol%          | 261.31   |
| CNC-water 0.9vol%          | 260.0    |
| CNC-water 1.3vol%          | 260.41   |
| CNC-water-Triton X-100 0.1vol% | 261.76   |
| CNC-water-Triton X-100 0.5vol% | 266.72   |
| CNC-water-Triton X-100 0.9vol% | 267.62   |
| CNC-water-Triton X-100 1.3vol% | 268.00   |

Figure 7 shows the relative concentration \( C/C_0 \) comparison with and without surfactant for all the concentrations from day 0 to day 4. Relative concentration \( C/C_0 \) was used to illustrate the behavior of sedimentation, in which a perfect condition is 1 and a decreased value indicates agglomeration of nanoparticles, followed by sedimentation [17]. The results showed that most of the samples decrease in relative concentration throughout the days but significantly drop at day 4. Therefore, the thermal properties measurement will be conducted in three days after the preparation of the samples. Furthermore, the results showed that the sample without surfactant has a lower relative concentration compared to the sample with surfactant. This shows that samples with surfactant have a higher relative concentration \( C/C_0 \) compare to those without surfactant. This was because the steric stabilization from
Triton X-100 managed to prevent significant agglomeration and sedimentation. Therefore, the absorbance drop can be maintained.

![Graphs showing absorbance drop between with and without surfactant for different concentrations](image)

**Figure 7.** Absorbance drop between with and without surfactant for (a) 0.1% vol%, (b) 0.5 vol%, (c) 0.9 vol%, and (d) 1.3 vol%.

3.2. Thermophysical properties

3.2.1. Thermal conductivity

Thermal conductivity analysis had been done to study the thermal performance of nanocellulose for heat transfer application. For the thermal conductivity analysis, only the samples with surfactants will be used due to better stability compared to samples without surfactant. Figure 8 shows the results of thermal conductivity for all concentrations compared to distilled water. At 30°C, there was no significant difference in thermal conductivity within all concentrations compared to distilled water. As the temperature increases, all the samples increased in thermal conductivity. This was because as the temperature increases, the kinetic energy of the particles increased. Due to the Brownian motion effect, the collision of suspended nanoparticles with molecules in the base fluid increased as the temperature increase [18, 19]. Most of the researchers, reviewed by Yang et al. [20] and Ahmadi et al. [21] agree that increasing the temperature of nanofluids results in higher thermal conductivity of nanofluids.

Furthermore, nanomaterial suspension causes the formation of the interfacial layer between nanomaterial and base fluid. This interfacial layer acts as a thermal bridge by reducing thermal resistance for better thermal conductivity improvement [22, 23]. There were some reading errors due to the high percentage error because of high temperature and low viscosity at 30°C for 0.5 vol% for significant drop and distilled water readings for significantly increased reading. However, Jiang et al. [24] mention that
temperature increases causing a reduction in thermal conductivity due to the increase in interfacial thermal resistance.

Although all samples had similar thermal conductivity at 30°C, sample 1.3vol% had a lower thermal conductivity. This was because in some cases, Tsai et al. [9] mentioned that high viscosity of based fluid reduces the Brownian motion of suspended nanoparticles. In this case, the “jelly-like” CNC which has high viscosity reduces the Brownian motion of the sample 1.3vol%. Therefore, the optimum concentration was important to have the best thermal conductivity rate of CNC-water/Triton X-100 samples. From figure 8, the highest reading of thermal conductivity was 1.224W/m.K for 0.5vol% at 40°C. Furthermore, the effective thermal conductivity achieved was 1.301 for 0.5vol% at 40°C compared with distilled water. Therefore, 0.5vol% and 40°C was the optimum parameter for best thermal conductivity reading of CNC-water/Triton X-100.

![Figure 8. Thermal conductivity of CNC-water/Triton X-100 for all concentrations](image)

4. Conclusion
The experimental investigation had been done to uncover the effect of surfactant on the stability of nanocellulose and its thermophysical properties. Triton X-100 was used as a surfactant with nanocellulose as its non-ionic surfactant properties. Steric stabilization was achieved as the samples with Triton X-100 has a higher relative concentration (C/Co). Furthermore, ultrasonication techniques also increases the stability of the samples. For the thermal conductivity analysis, the highest reading of thermal conductivity was 1.224W/m.K for 0.5vol% at 40°C and the effective thermal conductivity achieved was 1.301. Therefore, 0.5vol% and 40°C was the optimum parameter for best thermal conductivity reading of CNC-water/Triton X-100.

Further analysis can be done by using other stability analysis such as transmittance, or the Dynamic Light Scattering(DLS) technique. In addition, further thermal conductivity analysis can be done for higher temperature 50°C and above using lower percentage error equipment. Furthermore, other thermophysical analysis that can be done such as viscosity, specific heat capacity, and density to understand the behavior of nanocellulose with surfactant.

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