

SEPARATION OF NANOPARTICLES FROM NANOPARTICLE ENHANCED PHASE CHANGE MATERIALS

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ABSTRACT

A nano-colloid, referred as nanoparticle enhanced phase change material (NEPCM) is used to store heat energy. Using phase change mechanism, i.e., melting and solidifying, NEPCM stores and releases heat energy as per requirement. Nanoparticles are used as a means to enhance the thermal conductivity of the base fluid of the NEPCM. After repeated phase change cycles, NEPCM should be replenished. Since the disposal of the used NEPCM into the environment without any treatment possess environmental and health hazards it is necessary to develop technologies to separate the nanoparticles from the NEPCM before disposal. In this paper, several separation methods, such as: distillation, chemical destabilization, and centrifugation, yielding complete or partial separation, is evaluated and presented. The effectiveness of the separation methods have been analysed using Scanning Transmission Electron Microscopy (STEM).

INTRODUCTION

Phase change materials (PCM) are used in many energy (heat) storage applications where energy is stored (as latent heat of fusion) by melting the PCM and is released during solidification. Dispersing highly-conductive nanoparticles into the PCM enhances the effective thermal conductivity of the PCM, which in turn significantly improves the energy storage capability. The resulting colloidal mixture with the nanoparticles in suspension is referred to as nanoparticle enhanced phase change materials (NEPCM). A commonly used PCM for energy storage application is the family of paraffins (C_nH_{2n+2}). Mixing copper oxide (CuO) nanoparticles (treated with surfactants for stability) in paraffin produces a stable and highly conductive NEPCM for energy storage. However, after long term application cycles, the functionality of the NEPCM deteriorates and it is required to replace it with fresh supply. Disposal of the used NEPCM containing the nanoparticles is a matter of great concern as it cannot be discarded directly into the environment because of the short and long term environmental and health hazards [1, 2, 3, 4]. Due to widespread application potential of NEPCM, it is very important to develop proper technology to separate the nanoparticles before the disposal of the NEPCM. This is the motivation behind the present study.

Colloidal mixture (Fig.1) of dodecane ($C_{12}H_{26}$) and spherical CuO nanoparticles (1% - 10% mass fraction and size distribution of 5 - 15 nm) is considered. Various efficient and economic methods for separating the nanoparticles from the nanocolloid have been attempted. The identified viable methods include; (i) distillation under atmospheric and/or reduced pressure, (ii) physical filtration, (iii) destabilization of the nanoparticles by adding chemical agents thereby inducing gravitational precipitation, and (iv) very high speed centrifugation. These processes can be applied individually or in succession/combination. Successful results are obtained by attempting the following



Fig. 1. 100 ml 1% (by mass) NEPCM

methods: distillation under atmospheric pressure and vacuum, destabilization of nanoparticles using alcohol mixture, destabilization of nanoparticles using strong base, and ultrahigh speed centrifugation. This paper reports the methods followed and data obtained after trials. The analysis done to prove the effectiveness of the separation processes using STEM is also presented.

Keywords: Nanoparticle enhanced phase change materials, nanofluid, nanocolloid, PCM, NEPCM

SEPARATION METHODS

Distillation at Atmospheric Pressure and under Vacuum

In its simplest form, the direct distillation [5] is the process of heating the NEPCM (nanocolloid) in a flask at atmospheric pressure where the base fluid is vaporized followed by condensation in a condenser which is collected as distillate leaving behind nanoparticles as residue in the heating flask from where it can be collected.

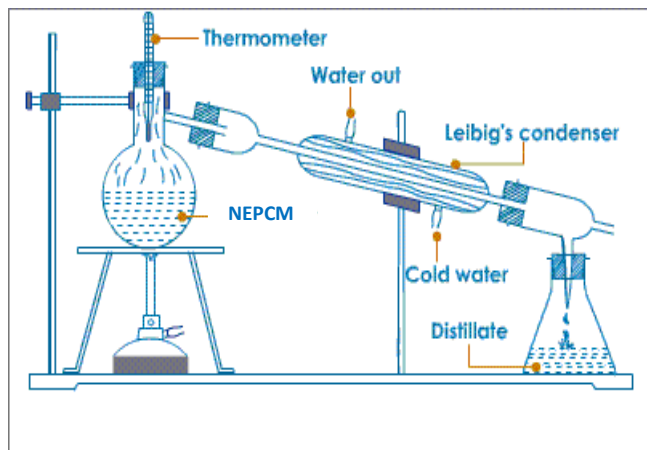


Fig. 2. Atmospheric distillation process set up.

A schematic of the distillation process is shown in Figure 2. Even though direct distillation is simple and convenient process, it has two major drawbacks: it runs slow and demands higher energy input. On the other hand, distillation at reduced pressure or vacuum is more efficient and faster.

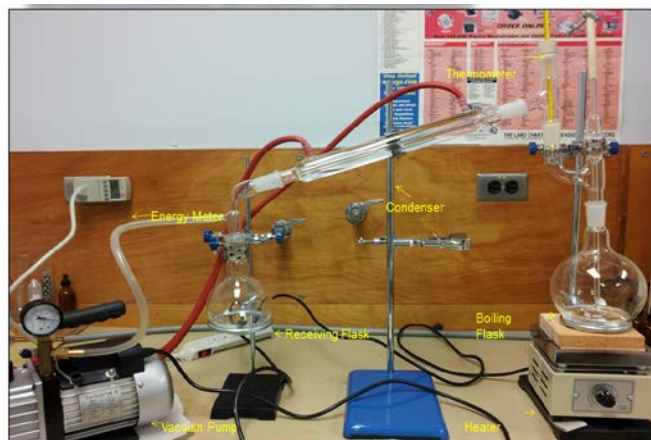


Fig. 3. Vacuum distillation setup.

Fig. 3 shows the set-up of vacuum distillation used for experiments. The process followed for the vacuum distillation is very similar to that of conventional distillation procedure except that the system is kept under vacuum using a 1.5 HP rotary vacuum pump. The glass-ware and equipment used were bought from Mountain Home Biological [6]. All standard safety measures and procedures were followed to conduct trials. The trials were conducted for different volumes of nanofluid containing nanoparticles at different mass fractions. The vacuum distillation was carried out at 33.6 kPa (absolute) which is about one-third of the atmospheric pressure.

A comparison of both atmospheric pressure and vacuum distillation processes is presented in Fig 4 and 5 from which it is evident that the vacuum distillation is much faster and

energy efficient than atmospheric pressure distillation. Based on quantitative analysis it is found that vacuum distillation consumes about 60% less energy and time for the same volume and mass concentration of nanofluid distilled.

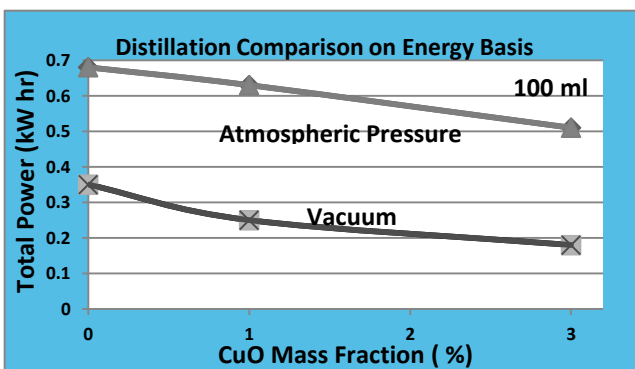


Fig. 4. Distillation comparison on energy basis.

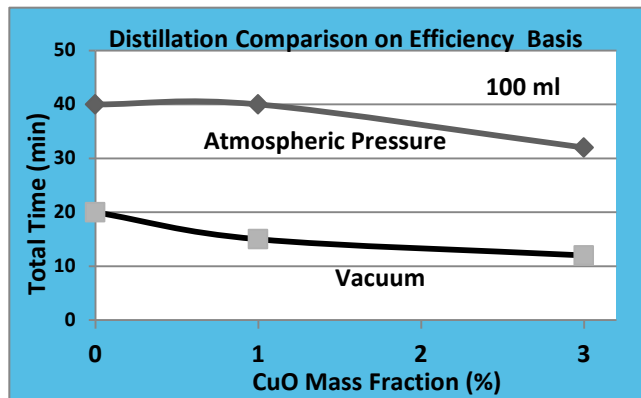


Fig. 5. Distillation comparison on Efficiency basis.

The NEPCM samples before and after distillation were analyzed by electron microscopy and compared to verify if residual trace of nanoparticle is present in the distillate. Fig 6(a) shows STEM image of the 99% pure technical grade dodecane structure which has been used as a base fluid for NEPCM preparation. The carbon web structure of dodecane is clearly discernible from 0.5% (by mass) concentration of the CuO nanoparticles. The lump of nanoparticles sticking to the carbon web structure is clearly visible in the image in Fig 6(a). The two images in Figs. 6(a) and (b) were compared with the STEM images of the distillate. Fig 6(c) shows the image of the distillate collected from the atmospheric pressure distillation while Fig. 6(d) shows the image of the distillate collected from the vacuum distillation. No trace of the nanoparticle is detected in the distillate in these images asserting that the distillation is a successful process for the separation of nanoparticles from the NEPCM.

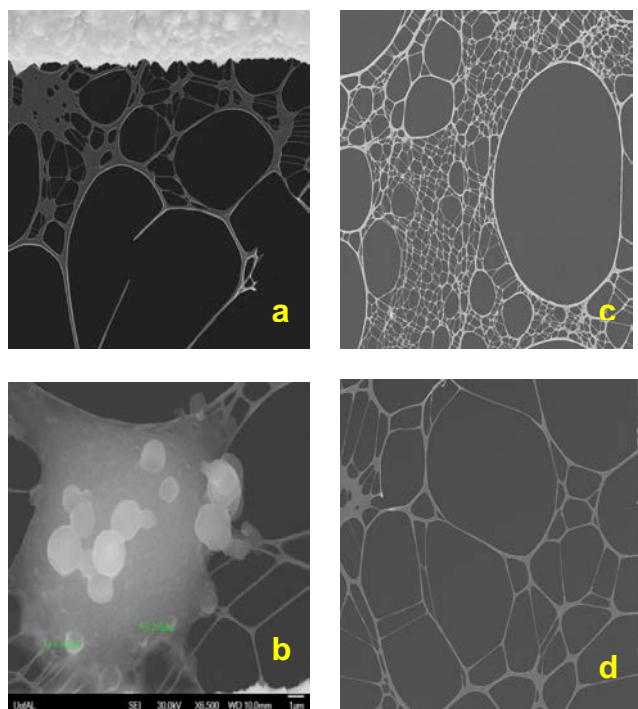
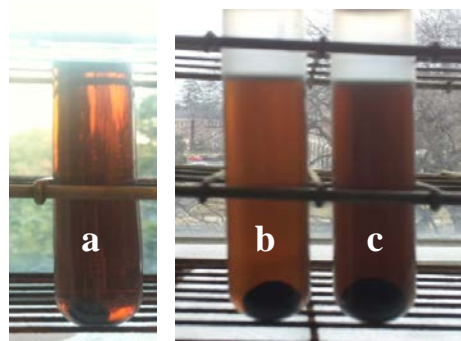


Fig. 6. Scanning Transmission Electron Microscope (STEM) images of: a) Dodecane, b) NEPCM, c) Distillate after atmospheric pressure distillation, d) Distillate after vacuum distillation.images.

Ultra-Centrifugation

Due to the density difference of the CuO nanoparticles (6.31 gm/cm^3) and dodecane (0.753 gm/cm^3) it was anticipated that centrifugation would lead to precipitation of the nanoparticles. At speed of up to 10,000 rpm, no sedimentation was observed for centrifugation duration of 30 minutes. At higher speed (15,000 rpm, i.e., 27,820 X gravity and up), nanoparticles started to sediment showing a trend of increasing sedimentation with increasing speed. Fig. 7 show the nanoparticle precipitation after centrifugation at different speeds and duration for different



- a) 12 ml 0.5 % conc.15,000 RPM (27,820 x g),4hrs
- b) 13 ml 2 % conc 18,000 RPM(40,173 x g),19.5hrs
- c) 13 ml 5 % conc 18,000 RPM(40,173 x g),19.5hrs

Fig. 7 Centrifugation Trial Results

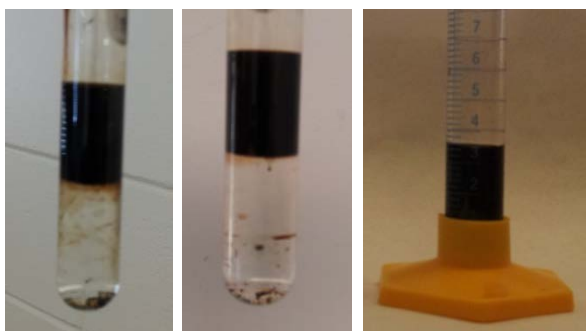
concentration. It is seen that centrifugation could not precipitate all of the nanoparticles from the given sample volume. This is due to the fact that the nanoparticles are treated with stabilizing surfactant (Oleic Acid , $\text{C}_{18}\text{H}_{34}\text{O}_2$) which produces ligands with string like structures on the particle surfaces. The ligands acts as stabilizing agent and prevents any precipitation or sedimentation. In order to quantify the particle removal efficiency of the centrifugation trials, a weight basis analysis was done by neglecting the volume occupied by individual nanoparticles. The efficiency is estimated by measuring the weight of the same volume of the NEPCM before and after centrifugation. Table 1 below shows the separation efficiencies of various trials.

Table 1. Separation efficiency of the centrifugation.

NEPCM Conc (by mass)	Vol(ml) Used to measure Efficiency	Separation Efficiency(%)
0.5 %	3	58.68
2.0 %	5	69.15
5.0 %	5	78.42

Destabilization using Alcohol Mixture

As mentioned in the previous section, the stabilizing ligands on the particle surfaces (surfactants) are made of oleic acid. Since this is soluble in some alcohols, it was perceived that, if the NEPCM is vigorously mixed/shaken with alcohol mixtures, the sodium oleate will get dissolved and removed from the particle surfaces thereby reducing the suspension stability of the particles and the precipitation of the particles will be easier and faster. After attempting some trials, it was found that a 50-50% mixture of propanol and methanol has a capacity to dissolve ligands. In this trial, equal volume of alcohol mixture and NEPCM were added into a test tube and were shaken for 30 mins at 450 Hz in a shaker unit.After shaking it was observed that the test tube volume occupied by the alcohol mixture increases substantially. This is mainly because alcohol mixture breaks through the stabilizing ligands of oleic acid thereby liberating the nanoparticles from the nanofluid and also making the dodecane (base fluid) to get dissolved in alcohol mixture. As alcohol mixture and dodecane are of same color they form a large volume of the fluid after shaking. This also can be interpreted as the above procedure leads to more concentrated nanofluid. Encouraged by this trial,5 ml of NEPCM (containing 0.5% mass fraction of nanoparticles) was added to 5 ml of alcohol mixture and experiment was repeated. Fig. 8 shows the results of first step after shaking at 450 Hz for 30 min. The concentrated nanofluid after shaking was pipetted out and was found to be 3.75 ml in volume. Using this concentrated 3.75 ml volume of the NEPCM, the experiment was repeated again adding another 5 ml of alcohol mixture and it was found that the nanofluid got concentrated to 2.5 ml as shown in step 2 of Fig. 8.



Before Shaking After Shaking NEPCM vol ~ 3.75 ml

Step 1: Results in 3.75ml NEPCM

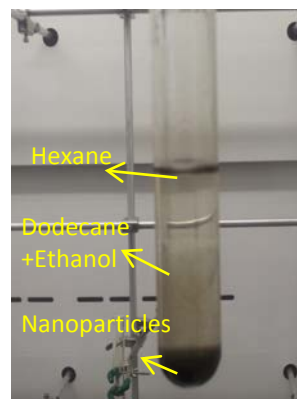
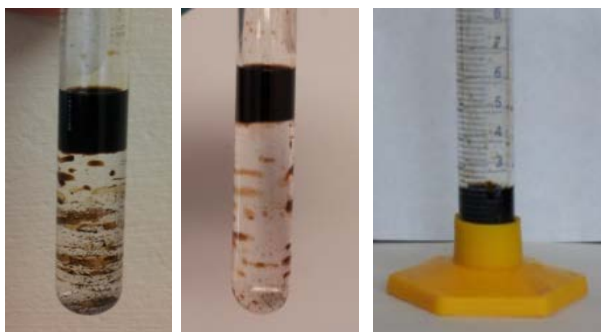


Fig 9. Nanoparticle destabilization using conc. Base.



Before Shaking After Shaking NEPCM vol ~ 2.5 ml

Step 2 : Results in 2.5 ml NEPCM

Fig. 8 Nanoparticle destabilization using alcohol mixture

CONCLUSION

Various methods for separating CuO nano particles from the NEPCM is tried. Of the four presented methods, three bring separation of nanoparticles primarily by breaking or dissolving the stabilizing ligands while distillation separates nanoparticles by evaporating the base fluid and leaving behind nanoparticles as impurities. These methods can be used exclusively or a combination may be used in succession for complete separation of the nanoparticles from the base fluid.

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Destabilization using Concentrated Base

In this trial, 3 ml of aqueous potassium hydroxide (KOH), 5 ml of NEPCM and 1 ml of ethanol was mixed in a test-tube and shaken for 10 secs. The result is shown in Fig 9, which shows accumulation of precipitated nanoparticles at the bottom followed by a layer of dodecane and a top layer of ethanol and hexane. The hexane was added later to improve visibility of layers.

Based on theoretical chemical analysis it is deduced that that KOH is causing stabilizer oleic acid to disintegrate from nanoparticle's surface by replacing previously attached oleate group with OH as shown in reaction below. This eventually results in loss of particle stability which leads to destabilization of nanoparticles.

