Phase change dispersion, potentially a new class of heat transfer fluids

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Abstract. The authors present values and an application of a phase change dispersion, where the dispersed phase change material within water changes from solid to liquid while absorbing heat and changes from liquid to solid while releasing heat at constant temperature. The phase change enthalpy increases the “apparent specific heat capacity” significantly in comparison to water. As the heat transfer takes place at constant temperature, the heat transfer fluid itself remains at constant temperature while absorbing heat. Isothermal heating and cooling of devices with a liquid is feasible.

1. Introduction

Thermal energy can be stored in form of latent heat using a phase change material (PCM). Melting as well as solidifying takes place at an almost constant temperature by storing or releasing heat at a certain temperature level, which makes PCM a good option for systems that require a temperature to remain on a constant level [1], [2].

A dispersion with a PCM as dispersed phase and a continuous phase, for instance water, is called a phase change dispersion (PCD). It could possibly be a solution for applications as isothermal heat transfer fluid for machine tools. The state of the dispersed material changes from liquid to solid and back at the specific PCM’s phase change temperature. To clarify the terminology, all the different kind of emulsions or suspensions with names like phase change emulsion (PCE) [3] or phase change slurry (PCS) [4] are henceforth labelled under the collective term phase change dispersion.

PCD properties as particle size distribution, thermal characteristics, viscosity and stability depend largely on the content of dispersed phase and included chemical agents [5][6]. The stability for instance, which indicates if or for how long the PCM particles within the PCD contain its shape, can be controlled by adjusting the drop size distribution, which is mainly influenced by the type and amount of emulsifier. As shown in Figure 1, the emulsifier creates a boundary layer around the PCM to prevent destabilizing effects as coalescence, creaming and aggregation.

Figure 1. Model of a dispersed PCM and functional chemical agents within a PCD.
Most recent publications on PCD addressed problems and opportunities for dispersions in general or for specific applications. Such as [3], with emphasizing on supercooling, the need of a wide phase change temperature range and the stability in general. Within [4][7][8], a summary on different PCD in order to evaluate the advantages and disadvantages, as well as to determine the boundary of each application, is given.

1.1. Envisaged Application
Modern machine tools have high precision requirements [9]. For the application of high performance spindles, in terms of thermal properties, it is required to have a constant temperature over the whole cooling area as well as a cooling agent which can be pumped through the cooling channels. Therefore, the application of a PCD is suggested [10].

1.2. Goals and Procedure
Various PCD with different phase change temperatures and formulations were produced in lab and production scale in order to determine how to produce and test an optimal PCD. Those were studied regarding their viscosity, particle size distribution, stability and fundamental thermodynamic properties. The experiences gained out of these experiments were used to develop an optimized formulation for a PCD with the required phase change temperature of 24°C.

In summary, the goal was to develop a PCD with:
- High stability
- Low supercooling
- High phase change enthalpy (increasing with content of dispersed phase)
- High heat transfer coefficient (decreasing with content of dispersed phase)

2. Experimental Setup

2.1. Formulation
A lot of different components and combinations of mass fractions were considered for finding the ideal formulation. For all samples, the major component of the PCD, the continuous phase, was water. The dispersed phase consists of a mixture of organic chemicals with paraffin (RT25HC) as main component. The emulsions were produced with different formulations of emulsifiers. An applicable emulsifier is a mixture of C\textsubscript{16} to C\textsubscript{18} partially ethoxylated alcohols which was used for increasing the stability of the PCD. To prevent supercooling, the higher melting myristic acid is added as a nucleation agent (0.5 to 5 % mass fraction). The concentration of emulsifiers varies from 1 to 8 % mass fraction in the different samples.

For producing an emulsion, rotor-stator based homogenizers are common practice. A rotor-stator type homogenizer with shear rates from 8’800 to 11’000 s\textsuperscript{-1} was used for the experiments. The homogenizing time varied between 1 and 10 min.
2.2. Thermal Properties

2.2.1. Supercooling. When a phase change from liquid to solid state takes place, a new molecular structure around a nucleus is formed. The creation of such a nucleus often demands the transfer of energy, since a new surface has to be built. The resulting deviation between melting and freezing temperature of a material is called supercooling, a well-known phenomenon for PCD [3][11]. However, the supercooling itself is not only a material property; its magnitude is system-dependent, influenced among other things by the sample size and its purity.

Reducing supercooling is important for PCD and their applications [7]. There are several approaches to induce an early nucleation and therefore to reduce supercooling. An applied method is to add special additives, also called nucleates, to the PCM to enforce heterogeneous nucleation e.g. with myristic acid [10].

2.2.2. Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) is used to measure the phase change enthalpy of the different components and the formulations. A DSC823e from Mettler Toledo was used, applying a “heat exchange calorimetry” to determine the heat exchange between ambient and sample as well as ambient and reference via thermal resistance [12].

A characteristic associated with DSC measurements is a distinctly visible supercooling of the samples as e.g. shown in Figure 6. However, the extent of supercooling occurring within a PCD in operation cannot be deduced directly from a standard DSC measurement. These two systems, DSC measurement and PCD in operation, are not compatible since they differ too much regarding the sample size and heat transfer condition.

![Figure 2](image1). Left: Test stand for measuring supercooling effects. Right: Close-up of glass vessel and stirrer.  

![Figure 3](image2). Typical T-History of a PCD with a heating rate of 0.5 K/min.

2.2.3. T-History Measurement. Since the influence of the “real scale” on the supercooling is important for the project, a method to investigate supercooling in larger quantities of PCD was developed. As the PCD is pumped through channels, friction and liquid flow may induce nucleation effects. A small sample within a DSC may show supercooling whereas in practical use supercooling might not occur that distinctive. Therefore, a test unit was developed in order to perform representative measurements.

Figure 2 shows the test rig used for the macroscopic temperature-history (T-History) measurement of PCD. A sample of about 100 ml is filled into a glass vessel, which is inserted into a bath with variable temperature. This way, the PCD temperature is determined by the heat transfer from bath to emulsion and vice versa as well as from the melting and freezing temperature. Both temperatures (bath and PCD) are measured continuously. To “imitate” a PCD flow similar to the application and increase the heat flow in general, a stirrer with a rotational speed of 100 min⁻¹ was employed (see Figure 2,
right side). The shaped stirrer ensures a good mixing and realistic shear force of the dispersion in order to avoid local freezing of the emulsion at the glass vessel surface and obtain a uniform temperature profile in the emulsion. During phase change, the PCD temperature follows the bath temperature with a delay. The temperature difference between bath and PCD indicates precisely melting and freezing points (see Figure 3).

2.3. Rheology
To determine the rheology of PCD formulations, a HAAKE Viscotest 550 was used. It is important to obtain empirical values of the viscosity of the PCD under operating condition, which are particularly dependent on the content of dispersed phase, shear rate and temperature.

2.4. Particle Size Distribution
The particle size distribution (PSD) is useful to determine the quality of a dispersion in general. Small particles/drops and a narrow drop size distribution indicate stability [1][13][9]. Measuring the particle size is a valuable tool for controlling the quality of dispersions. A Beckman Coulter LS 13320 with Polarization Intensity Differential Scattering (PIDS) and Laser Diffraction is used. The measuring range lies between 0.04 – 2’000 μm.

2.5. Stability Analysis
To determine the long-term stability [14] of PCD, the LUMiSizer [15], a centrifuge with transmission detection was used.

3. Modelling Properties
To calculate the thermal behavior of a system using standard CFD modelling, the corresponding properties to be used within the models need to be defined. A practical approach is the quasi homogeneous model [16]. The properties of the individual continuous and dispersed phase are combined into one (homogenous) phase with properties that reflect correctly the overall system behavior. Hence, it is necessary to define the corresponding values for the thermal conductivity λ, the heat capacity \( c_p \) and the density \( \rho \). The properties have to be known for the single substances as well as the dispersion in dependence on the content of dispersed phase \( \psi \).

3.1. Properties of pure Substances
Within literature a vast collection of deviating values for PCM is available [1][2]. Reliable sources were considered and important values like melting point and phase change enthalpy were measured. Non obtainable values of minor importance were assumed according to properties of substances with similar chemical structure. The results are combined in Table 1.

| Substance | \( T_{onset} \) [°C] | \( T_p \) [°C] | \( \Delta T_{mtr} \) [K] | \( \rho_s \) [kg/m³] | \( \rho_l \) [kg/m³] | \( \lambda_c \) [W/mK] | \( \lambda_l \) [W/mK] | \( c_{p,s} \) [kJ/kgK] | \( c_{p,l} \) [kJ/kgK] | \( \Delta h_m \) [kJ/kg] | Refs. |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------|
| Water     | 0               | 3               | 4               | 917             | 1000            | 2.25            | 0.57            | 2.04            | 4.203           | 333.6           | [16]   |
| RT25HC    | 22.9            | 26.5            | 4               | 880            | 760             | 0.2            | 0.23            | 2.0            | 2.28           | 209            | [16]   |
| Myristic acid | 53.6          | 55.0            | 5               | 990            | 862             | 0.15            | 0.16            | 2.18            | 2.15           | 194            | [17]   |

*Own measurement. **Assumption.

3.2. Apparent specific Heat Capacity
PCD stores or releases heat in two different ways, first, by the continuous and dispersed phase in sensible heat and second, by the dispersed phase, the PCM, in latent heat.

For the use in model calculations, it is beneficial to combine these two effects since they are overlapping. The expression “apparent specific heat capacity” for multiphase materials has been established by [18].
The apparent heat capacity $c_{p,PCD}$ can be calculated according to Equation (1).

$$c_{p,PCD} = (1 - \psi) c_{p, H_2O} + \psi \frac{\Delta h_{m,c}}{\Delta T_c}$$ (1)

The apparent heat capacity is dependent on the content of dispersed phase $\psi$, the considered temperature difference $\Delta T_c$ and the considered enthalpy of fusion $\Delta h_{m,c}$. It is important to distinguish between considered temperature difference $\Delta T_c$ and the entire melting temperature range $\Delta T_{mtr}$, because the energy stored during a phase change is dependent on the actual temperature as well as the applied temperature difference, as observable in the DSC measurements.

The specific use of the PCD in the application of isothermal cooling has to consider that the “temperature range of application” is smaller than the entire melting temperature range. The absorbed enthalpy during melting depicted vs. the temperature has simplified a triangular shape. At its “tip”, the absorbed heat per temperature difference is at most. We suggest therefore considering this situation by the following approach:

The calculation of the considered enthalpy of fusion $\Delta h_{m,c}$ is according to Equation (2) using a correction factor $k_T$ and the enthalpy of fusion for the entire melting temperature range $\Delta h_{m,mtr}$, which includes the sensible and latent heat of the PCM within the applied temperature range.

$$\Delta h_{m,c}(\Delta T) = k_T(\Delta T) \Delta h_{m,mtr}$$ (2)

The correction factor $k_T$ is based on the consideration that a generic DSC diagram (as shown in Section 4) with one distinct melting temperature can be approximated by an isosceles triangle, as shown in Figure 4. The base correlates to $\Delta T_{mtr}$ and the total area under the triangle corresponds to $\Delta h_{m,mtr}$. By selecting a section representing $\Delta T_c$ around the peak temperature $T_p$, an area (dark grey) is obtained which represents the value $\Delta h_{m,c}$. By taking the quotient of these two areas, the dimensionless correction factor $k_T$ is determined. It is important to notice that $k_T$ is not proportional to $\Delta T$. As a result, the apparent heat capacity increases with decreasing temperature difference and increasing phase fraction, as shown in Figure 5.

As can be seen in Figure 5, the application of a small temperature range, corresponding to isothermal operation is beneficial. At phase contents around 20 % e.g. the apparent specific heat capacity of a PCD is increased by a factor of 3 to 5 in comparison to water.

**Figure 4.** Applied model for calculating the correction factor $k_T$.

**Figure 5.** Apparent heat capacity in dependence on the content of dispersed phase $\psi$.

### 3.3. Outlook

For non-CFD calculations based on Nusselt-correlations [16], the still unsolved question is whether such correlations are valid for PCD and how the Prandtl number has to be calculated.

Furthermore, it has to be considered that a decreasing temperature difference (as shown in Figure 4) results of course in a lower amount of heat that can be stored at all. This means a solution to the optimization problem, the optimal temperature difference, of weighting apparent heat capacity and total amount of stored heat has to be found.
4. Experimental Results

4.1. Phase Change Enthalpy

Figure 6 shows a DSC measurement comparing four different formulations. For A, B and C formulations according to Section 2.1 were used with RT25HC as PCM with increasing content of dispersed phase and increasing content of nucleation agent. The precise formulations are given in [10]. The phase change enthalpy corresponds to the surface area under the “peak”. It is noticeable that including a higher amount of PCM results in an increase in phase change enthalpy but also causes a shift of the melting temperature. Graph D is a reference measurement where a different PCM, technically pure Octadecane, with otherwise the same formulation as C has been used.

![Figure 6](image)

**Figure 6.** DSC measurement with increasing content of dispersed phase (A,B,C,D) and different PCM with otherwise same formulation as C. All measurement taken at a heating rate of 2 K min⁻¹.

4.2. Supercooling

For another set of PCD formulations, the T-History analysis was implemented. Figure 7 shows the results of the T-History-measurement. The three formulations have an adjustable configuration of myristic acid. It can be observed that the supercooling decreases from left to right in step with the increasing amount of myristic acid. Hence, it is possible to reduce supercooling at a comparable drop size distribution by adjusting the concentration of the nucleation agent.

![Figure 7](image)

**Figure 7.** Result for T-History measurement for different configurations with increasing amount of the nucleation agent from left to right. Square: Freezing. Circle: Melting.
4.3. Rheology

PCD below their melting temperature show non-Newtonian behavior. Relevant shear rates for the envisaged application lie between 50 and 100 s\(^{-1}\). Within this range, the viscosity remains nearly constant, as shown in Figure 8. Increasing the sample temperature, on the contrary, results in a noticeable viscosity decrease (values not shown). Caused, firstly, due to decreasing viscosity of the continuous phase, and secondly, by changing from suspension to emulsion once the melting point of the PCD is exceeded.

![Figure 8. Viscosity of PCD samples at 22°C with varying content of dispersed phase \(\psi\).](image)

![Figure 9. PSD as function of the emulsifier mass fraction at a shear rate of 20'000 s\(^{-1}\) and 5 min dispersing time.](image)

4.4. Particle Size Distribution, PSD

The particle size distribution within a dispersion depends mainly on formulation (emulsifier), shear rate and shear intensity (energy input) [4][7][8].

Within Figure 9, the influence of the emulsifier concentration is shown. As can be seen, the increase in emulsifier content reduces the mean particle size as well as the maximum particle size. In Figure 10, the influence of shear rate and dispersing time is illustrated. The higher the shear rate and the longer the dispersing time, the smaller the resulting particles.

![Figure 10. PSD as function of shear rate and dispersing time with 8% emulsifier.](image)

5. Discussion and Outlook

Phase change dispersions enable the absorption and release of heat at constant temperature. In comparison to water, the specific heat capacity (factor 2-10) but also the viscosity (factor 2-100) is significantly higher. The largest potential is shown in applications, where an isothermal device enables
a significant advantage in quality. The presented formulations have the necessary quality with respect to particle size distribution, stability and supercooling.

The influence of the emulsifier on PCD behavior is of the essence. Smart formulations with appropriate emulsifiers will allow for formulations with lower viscosity, which is in general an advantage for pressure drop and heat transfer. On the other hand, low viscosity is encouraging instability by creaming. This effect again can be limited by small droplet sizes. However, small droplet sizes support supercooling. Emulsifiers with strong interaction with the PCM are advantageous for stable dispersions, but the melting temperature is reduced and the melting temperature range is extended.

Further comprehensive research is necessary to predict such effects and finally to find formulations, being suitable for the respective applications. This leads to an optimization problem: The pressure drop caused by viscosity and the heat capacity have to be modelled and will result in an optimal phase content $\psi$. A proper understanding of heat transfer coefficients as function of viscosity and PCD formulation is still outstanding and part of ongoing research of the authors.

6. References

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