DEVELOPMENT OF
ADVANCED LOW-TEMPERATURE HEAT TRANSFER FLUIDS
FOR DISTRICT HEATING AND COOLING

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ABSTRACT

The feasibility of adding phase change materials (PCMs) and surfactants to the heat transfer fluids in district cooling systems was investigated. It increases the thermal capacity of the heat transfer fluid and therefore decreases the volume that needs to be pumped. It also increases the heat transfer rate, resulting in smaller heat exchangers. The thermal behavior of two potential PCMs, hexadecane and tetradecane paraffin wax, was experimentally evaluated. The heat of fusion of these materials is approximately 60% of that of ice. They exhibit no supercooling and are stable under repeated thermal cycling. While test results for laboratory grade materials showed good agreement with data in the literature, both melting point and heat of fusion for commercial grade hexadecane were found to be considerably lower than literature values. PCM/water mixtures were tested in a laboratory-scale test loop to determine heat transfer and flow resistance properties.

When using PCMs in district cooling systems, clogging of frozen PCM particles is one of the major problems to be overcome. In the present project it is proposed to minimize or prevent clogging by the addition of an emulsifier. Effects of the emulsifier on the mixture of water and hexadecane (a PCM) were studied. As the amount of the emulsifier was increased, the size of the solid PCM particles became smaller. When the size of the particles was small enough, they did not stick together or stick to the cold surface of a heat exchanger. The amount of emulsifier to produce this condition was determined.
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APPENDIX D: Effect of Emulsifier on PCM Particle Size
1. INTRODUCTION

This report covers the second year of a project on Advanced Heat Transfer Fluids for District Cooling. The objective of this project is to develop heat transfer fluids that (1) have improved heat transfer properties and (2) reduce the volume of fluid that needs to be pumped.

The approach taken is to add to the carrier fluid a large quantity (up to 25%) of a phase change material (PCM) whose phase-change or phase-transition (melting/freezing) temperature is between the send-out and the return temperature of conventional district cooling systems. The increased thermal capacity of the PCM/water mixture decreases the pumping volume required and therefore results in savings in pumping energy, which constitutes a large fraction of the total input energy of district cooling systems.

Better mixing of the carrier fluid due to the presence of solid particles tends to increase the convective heat transfer coefficient, which decreases the size of the heat exchangers required at both ends of a district cooling system. Previous work makes it probable that the addition of solid particles will not materially increase the pressure drop of the heat transfer fluid through pipes or heat exchangers. It is expected that the proposed heat transfer enhancement technique does not require any hardware retrofits or modification of heat exchangers and that it can be used concurrently with other passive or active heat transfer augmentation techniques.

Previous attempts to achieve these objectives have usually employed water/ice as the phase change material (Cleary et al 1990, Winter and Kooy 1991). This has the disadvantage of requiring lower evaporator temperatures at the compressor(s) resulting in increased power demand. The approach taken in the present project is to use a phase change material with a higher melting/freezing temperature than water/ice in order to avoid having the compressor work at lower temperatures than required for a conventional cooling system.

In order to maximize the saving in pumping energy that can be obtained from using a phase change material-water slurry as the primary heat transfer medium in a district cooling system, the
phase transition temperature of the PCM should be between 3°C (37 F) and 10°C (50 F), depending on the design temperature of the primary cooling loop. Its latent heat should be as high as possible, it should form a slurry with water, it should exhibit little or no supercooling, be stable under repeated thermal cycling, be inexpensive, and preferably be chemically inert and nontoxic. Paraffin wax satisfies most of these conditions, and it has been used as thermal storage material (Altman et al. 1973; Lane 1983). These waxes are well characterized. They consist of simple, long molecular chains of CH₂ units with a CH₃ unit at each end (Fig. 1). The exact phase transition temperature depends on the length of the chain, increasing with increasing chain length.

The desirable phase transition temperature for the district cooling application is straddled by the phase-transition temperatures of tetradecane (5.8°C, 42.4 F) and pentadecane (9.9°C, 49.8 F). Thus it seems plausible that a mixture of these two waxes may represent a good choice. Since pentadecane is relatively expensive, mixtures of hexadecane (phase transition temperature of 18.1°C, 64.6 F) with tetradecane were also believed to be worthy of investigation.

2. THERMAL PROPERTIES OF THE SELECTED PHASE CHANGE MATERIALS

2.1 Test Apparatus

A Differential Scanning Calorimeter (DSC) was used in connection with a Differential Thermal Analyzer (DTA) to determine melting points and heats of fusion of potential phase change materials. Details of the test apparatus are presented in Appendix A, Fig. 1, page 2.

The apparatus was carefully calibrated as described in Appendix B, Figs. 2 through 4, pages 2 through 4.

2.2 Test Results

While the thermal properties of laboratory grade phase change materials measured under this project agreed well with data published in the literature (Lane 1986, Handbook of Physics and
Chemistry 1986), it was found that the properties of commercial (also called technical) grade materials were significantly lower than the properties of the laboratory grades. Since the cost of laboratory grade material is prohibitively high, only commercial grade materials would be used in any large-scale application of PCMs to district heating. Therefore, later testing was performed on commercial grade materials.

The effect on melting point and heat of fusion of different mixes of tetradeccane and hexadecane are shown in Appendix B, Fig. 5, page 5. It was concluded from these test results that mixtures of these two substances in the ranges of 10% to 90% by weight exhibit multiple phase changes caused by molecular rearrangement (Fig. 2). In the ranges from 0 to 10% and from 90% to 100%, however, a single phase change is dominant. It is these ranges that are of interest for district cooling. Both melting temperatures and heats of fusion of the mixtures in these ranges are slightly lower than those of the pure substances. The melting temperature depression within the ranges of interest is theoretically predictable (see Appendix B, Figs. 8 and 9, pages 7 through 9). Test results for melting temperatures and heats of fusion for various mixtures of laboratory and commercial grades hexadecane with laboratory grade tetradeccane are shown in Figs. 3 and 4, respectively. The difference in melting temperatures between the laboratory grade and the commercial grade materials is considerable: almost 5°C. While the difference in heats of fusion may be as large as one third, it is no larger than 20% in the ranges of interest. Based on the above heat of fusion data, the volumetric thermal capacity of a heat transfer fluid consisting of a PCM/water mixture is shown in Fig. 5. The percentage increase is larger for smaller temperature ranges, ΔT, between sendout and return temperatures.

3. PCM PARTICLE SIZE
3.1 Test Apparatus
A bench-type flow loop had been built under a previous contract consisting of a storage tank, a test cooling section, and a heating section, with an associated pumping system. Successful tests proved the basic feasibility of the concept of using n-alkanes to increase the thermal properties of heat transfer fluids suitable for district cooling.

A larger flow loop was then built in order to measure thermal and hydraulic properties of the PCM/water mixture (Appendix C, Fig. 6, page 3). The larger flow loop was rebuilt and improved in order to permit more accurate observation and data-taking in addition to longer run times (Appendix C, Fig. 7, page 4). From the operation of this loop it became apparent that the design of the cooling reservoir is highly important. It appears that freezing of the PCM should preferably take place inside, not outside, the cooling coil. Under certain conditions, the piping became clogged with frozen PCM particles.

3.2 Flow Loop Clogging

A major obstacle to the use of n-alkanes in water as a heat transfer fluid in a district cooling system is the clogging of the piping system through frozen PCM particles. In order to make it possible to use a PCM/water mixture, a reliable method of generating extremely small, non-sticking PCM particles must be developed. An emulsifier was used to minimize or prevent this phenomenon. The emulsifier consisted of linear alkylbenzene sulfonate, polyethoxylated fatty alcohol, and triethanolamine. The PCM used for this study was hexadecane. Although it would not be selected in an actual district heating system on account of its high melting point (18.1°C), this property makes it a convenient substance for studying the effect of adding an emulsifier. Since the chemistry of all the n-alkane waxes is similar, it is expected that results from hexadecane tests will be readily transferable to tetradecane and pentadecane, which are more suitable candidates for use in district cooling systems.
In a mixture of water and n-alkane the two materials are immiscible. The addition of an emulsifier reduces the size of the n-alkane particles and causes them to be suspended in the water. Since the emulsifier tends to increase the interfacial area of water and PCM, and since the interfacial area of small particles is larger than that of large particles, the size of the liquid particles of hexadecane becomes smaller as the amount of emulsifier is increased. This behavior was found to hold true in two types of experiments: direct contact heat exchange, and heat exchange in a copper heat exchanger. Details are given in Appendix D.

3.3 Use of Emulsifier

When no emulsifier was used, irregular, large lumps of solid hexadecane particles were formed as soon as the mixture was cooled below the freezing point of the PCM. The solidification started at a number of locations, and individual particles, once formed, quickly grew into large lumps. These lumps were very stiff and, if they are present in a flow loop, they will clog the loop immediately. As emulsifier was added to the water-hexadecane mixture, the size of the PCM particles became smaller. At an emulsifier concentration of 680 ppm or greater, the particles no longer stuck together to form clumps. Hence, it appears that there is a critical particle size below which the hexadecane particles do not stick together. When 3000 ppm of emulsifier were added, the particles became too small to be seen by the naked eye. The amount of emulsifier required to produce the critical value of particle size for a 25/75% mixture of hexadecane and water was found to be 680 ppm. In order to obtain uniform, stable solid particle suspensions, the amount of emulsifier should be greater than this value.

It is speculated that, when the particles are large, the inertial force of each particle is so large that it breaks the emulsified layer on the surface of the particle. Subsequently, the surface of the particle makes direct contact with other particles to form large lumps. When the particle is small, its inertial force is so small that it is repelled by the electric charge on the emulsified layer.
Thus the emulsified liquid particles of hexadecane are frozen to become suspended solid particles without sticking to each other.

4. PUBLICATIONS PREPARED UNDER THIS CONTRACT

Cho, Y.I., Choi, E., and Lorsch, H.G.
"Thermal Analysis of n-Alkane Phase Change Material Mixtures"
presented at the International Symposium on Fluids for District Heating
Copenhagen, April 1991
This paper is attached as Appendix B to this report.

Cho, Y.I., Choi, E., and Lorsch, H.G.
"A Novel Concept for Heat Transfer Fluids Used in District Cooling Systems"
presented at the Annual Meeting of the American Society of Heating, Refrigerating and Air-Conditioning Engineers
Indianapolis, IN, June 1991
This paper is attached as Appendix C to this report.

5. MEETINGS ATTENDED

The meeting of the IEA Advanced Transmission Fluids Expert Group held on June 21, 1991 in Toronto, Canada was attended by Dr. Lorsch.

Dr. Cho visited the University of Dortmund, Germany on April 8, 1991 where he was familiarized with the work on advanced heat transfer fluids being pursued at that university. The meeting of the IEA Advanced Transmission Fluids Expert Group held on April 9, 1991 in
Copenhagen, Denmark was attended by Dr. Cho. He presented a paper (see above) at that meeting.

Dr. Lorsch attended the annual meeting of the American Society of Heating, Refrigerating and Air-Conditioning Engineers, held on June 22-26, 1991 in Indianapolis, IN. At that meeting he presented a paper (see above) during a symposium on Advanced HVAC Fluid Technology Applicable to District Cooling. The paper gave rise to a lively question-and-answer period. The facility manager at the Dallas-Ft. Worth Airport, which contains a large district heating and cooling system, wanted to know the price of the recommended PCM. Other questions pertained to the size of the PCM particles used and whether the heat transfer data given included the effect of phase change., which they do. A professor from the University of New Mexico wanted to know why the drastic change in heat transfer from the laminar to the turbulent region does not also occur in the Fanning friction coefficient. A researcher from CBI mentioned that they had encountered clogging of their ice slurries at branching points; this corresponds to the build-up of solid PCM particles at the outlet of the surge tank when no or little surfactant was used in our PCM/water slurries. The paper as well as the questions and answers will be published in ASHRAE Transactions, vol. 97, part 2, 1991.

6. FUTURE WORK PLANNED UNDER A FOLLOW-ON CONTRACT

The work described in this report is continuing under a follow-on contract. It is planned to build a larger flow loop that will allow operation at higher Reynolds numbers than was previously possible. The heating and cooling sections of that loop will be instrumented with a large number of thermocouples. This will permit the determination of the progression of melting/freezing of the phase change material as the transfer fluid passes through a heat exchanger. A portion of this flow loop will be made of transparent material so that flow patterns can be observed.
The emulsifier tests previously performed with hexadecane will be repeated with a mixture of tetradecane and hexadecane that has a melting point suitable for district cooling systems. Heat transfer coefficients and pressure drops for this mixture will be measured.

7. REFERENCES


Handbook of Chemistry and Physics, 1986. The Chemical Rubber Co.


Figure 1. Molecular Structure of Selected n-alkanes (Paraffin Waxes)
Figure 2. Measured melting temperatures for mixtures of laboratory grade hexadecane and tetradecane
Figure 3 Measured melting temperatures for mixtures of laboratory grade tetradecane with laboratory grade and commercial grade hexadecane
Figure 4 Measured heats of fusion for mixtures of laboratory grade tetradecane with laboratory grade and commercial grade hexadecane.
Figure 5. Volumetric heat capacity of water/pentadecane slurries (ΔT=15°C)
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