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Experimental Phase Diagram of the Dodecane-Tridecane System as Phase Change Material in Cold Storage

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Highlights:

- $C_{12}H_{26}$ - $C_{13}H_{28}$ system has a congruent minimum-melting solid solution and polymorphs
- The minimum-freezing 17.7 mol% $C_{13}H_{28}$ blend (at -16 to -12 °C) is a potential PCM
- 17.7 mol% $C_{13}H_{28}$ blend freezes with an enthalpy of 165 kJ kg⁻¹ and no supercooling
- The system has a minimum-melting trend, but has no eutectic as literature proposed
- Extensive physicochemical studies needed to explain melting/freezing discrepancies

Abstract

Integrating thermal storage with phase change materials (PCMs) in refrigeration and air conditioning processes enables energy performance improvements. Herein, the experimental phase diagram of the alkanes system dodecane-tridecane ($C_{12}H_{26}$ - $C_{13}H_{28}$) is evaluated to find PCMs for freezing applications. For that, the Temperature-history method was coupled with a Tammann plot analysis. The obtained $C_{12}H_{26}$ - $C_{13}H_{28}$ phase diagram indicated a congruent minimum-melting solid solution and polymorphs. The minimum-melting liquidus and the polymorphs identified here, agree with previous literature. However, the system does not represent a eutectic, as previously was proposed. The minimum-melting composition is here identified within 15-20 mol% $C_{13}H_{28}$ compositions. The 17.7 mol% $C_{13}H_{28}$ is the narrowest minimum-melting composition among those analyzed, melting and freezing between -16 to -12 °C and -17 to -15 °C, with: the enthalpies 185 kJ kg⁻¹ and 165 kJ kg⁻¹; no supercooling; and only minor hysteresis. Hence, this blend has potential as a PCM in freezing refrigeration applications.

Keywords: *phase change material (PCM); $C_{12}H_{26}$ - $C_{13}H_{28}$ system; phase diagram; Temperature-history method; Tammann plot; minimum-melting*

Nomenclature

Symbols

c_p	Specific heat at constant pressure (kJ kg ⁻¹ K ⁻¹)
Δh	enthalpy change (kJ kg ⁻¹ or kJ mol ⁻¹)
h	enthalpy (kJ kg ⁻¹ or kJ mol ⁻¹)
t	time (s)
T	Temperature (°C)

Subscripts and superscripts

E	eutectic
e	end
M	melting
s	start
R	reference

Abbreviations

C ₁₂	Dodecane (C ₁₂ -H ₂₆)
C ₁₃	Tridecane (C ₁₃ -H ₂₈)
DSC	Differential Scanning Calorimetry
Fr	Freezing
FT-IR	Fourier-Transform Infra-red Spectroscopy
L	liquidus
M	Melting
PCM	Phase Change Material
R _i	Rotationally disordered orthorhombic phase
S	solidus
SS	stainless-steel/solid-solid phase change (as relevant)
TES	Thermal Energy Storage
T-History	Temperature-History
T _p	Triclinic phase
XRD	X-Ray Diffraction

1 Introduction

Energy efficiency, renewable energy integration, and energy management are all essential to combat climate change. Thermal energy storage (TES) is an effective alternative to achieve these goals, where one storage choice is with phase change materials (PCMs). PCMs have the competitive advantage of denser thermal storage capacities, in contrast to sensible heat/cold storage (Mehling and Cabeza, 2008). By integrating PCMs into refrigerators (Yusufoglu et al., 2015; Sonnenrein et al., 2015), air-conditioners (Huang et al., 2010; Poshtiri and Jafari, 2017), free cooling (Stritih and Butala, 2010; Osterman et al., 2012), and absorption/adsorption chillers (Osterman et al., 2012; Helm et al., 2009), load and power consumption minimization, renewable energy integration, efficiency and performance improvements, and cost reductions are achieved. Cold storage and transportation are responsible for a major share of CO₂ emissions, which, however, can be greatly alleviated by integrating with PCM-based storages (Oró et al., 2014).

Alkanes, many referred to as paraffins, are among PCMs which have reached commercialization. Alkanes have stable phase change, minimal supercooling, and good phase change enthalpies. They are also compatible with metals, altogether making them attractive as PCMs (Mehling and Cabeza, 2008). Their shortcomings include being of non-renewable origin, low thermal conductivities and incompatibility with plastics (Mehling and Cabeza, 2008). For their PCM-attractive features, alkanes have been extensively

evaluated in the PCM-context, as, pure components (e.g. Huang et al., 2010; Kenisarin, 2014; Şahan et al., 2015; Si et al., 2015; Navarro et al., 2016; Zhang et al., 2016; Fioretti et al., 2016; Arshad et al., 2017; Sattari et al., 2017) and blends (e.g. Choi et al., 1992; Espeau et al., 1996; Stolk et al., 1997; He et al., 1999; Ventolà et al., 2002; He et al., 2003; Mondieig et al., 2004; He et al., 2004; He, 2004; Ventolà et al., 2005; Yilmaz et al., 2009). A number of ideal blend compositions were proposed, including congruent melting solid solutions and eutectics (Gunasekara et al., 2017b). However, some of these blends evaluations have presented varying phase diagrams for the same system. The system dodecane-tridecane ($C_{12}H_{26}$ - $C_{13}H_{28}$) (Ventolà et al., 2002; Yilmaz et al., 2009), which could have a great potential for freezing in refrigeration applications, is one such example with major discrepancies on the proposed phase diagrams. In one study, based on only the liquidus, this system was derived as one increasing towards a temperature maximum (Yilmaz et al., 2009). In another study, it was deduced as a partially isomorphous system with a eutectic and a eutectoid in a detailed phase diagram (Ventolà et al., 2002).

The thermal and crystallographic characteristics of the pure dodecane ($C_{12}H_{26}$, C_{12} hereon) and tridecane ($C_{13}H_{28}$, C_{13} hereon) found in literature are summarized in Table 1. In even alkanes, the melting phase is an ordered triclinic phase, which is also true for C_{12} (Ventolà et al., 2002), and is denoted with T_p . Odd alkanes melt from a rotationally disordered orthorhombic phase, which is hence the same for C_{13} (Ventolà et al., 2002), and is denoted with R_i . Pure C_{13} in addition has a polymorphic phase at lower temperatures, and this is orthorhombic (a face centered Bravais lattice) (Mondieig et al., 2004; Yan et al., 2013). Such pure component characteristics are important when exploring blends, since these will affect their phase diagram.

Yilmaz et al. (2009) investigated the C_{12} - C_{13} system employing cooling curves acquired using a thermostat-bath and Differential Scanning Calorimetry (DSC). Thereby, the systems' onset (the starting) temperatures of freezing were deduced and were plotted as the liquidus, which, with increasing C_{13} content, increased to a temperature maximum, followed by a decrease (Yilmaz et al., 2009). The temperature maximum in the C_{12} - C_{13} phase diagram occurs at around -3 to -5 °C, at the composition 80% w/w C_{13} (~78.7 mol% C_{13}) and freezing with an enthalpy of 126 kJ kg⁻¹, based on DSC (Yilmaz et al., 2009).

Contrary to Yilmaz et al. (2009), Ventolà et al. (2002) identified the same system to be partially-isomorphous, with a eutectic at around 17 mol% C_{13} and -17 °C, and a eutectoid at lower temperatures. Their phase diagram deduction method was not explicitly described. However, it appears to involve the thermal properties, the crystallography of the pure components and two blends (30 and 50 mol% C_{13}), and thermodynamic modelling (Ventolà et al., 2002). The melting phase of the 30 and 50 mol% C_{13} were the same as that of pure C_{13} (i.e. R_i) (Ventolà et al., 2002). The phase boundary choices with respect to the onsets/offsets of the phase change peaks were unspecified. In the phase diagram (Ventolà et al., 2002), the eutectic isotherm and the solvus curves were indicated using discontinuous phase boundaries, although the reasons were not disclosed. The detailed methodology of this assessment was said to be explained elsewhere (Espeau, 1995), which however is unavailable in open literature. Furthermore, the eutectic enthalpy was not presented, but only the melting enthalpies of the 30 and 50 mol% C_{13} composition, each reported to be 146 kJ kg⁻¹ (Ventolà et al., 2002). The polymorph of pure C_{13} was identified by Ventolà et al. (2002) (c.f. Table 1), and was shown in the C_{12} - C_{13} phase diagram, as giving

rise to a eutectoid at lower temperatures. Neither study (Ventolà et al., 2002; Yilmaz et al., 2009), disclosed their investigated sample sizes, nor the system's hysteresis effects.

In order to explore potential PCM compositions for freezing applications, a thorough examination of the phase equilibrium is needed for the $C_{12}H_{26}$ - $C_{13}H_{28}$ system. The aim of the present work is thus to thoroughly establish its phase equilibrium through comprehensive thermal property evaluation including the Temperature-History (T-history) method (Chiu and Martin, 2012; Gunasekara et al., 2016; Gunasekara et al., 2017a) coupled with Tammann plots (Rycerz, 2013). Only with a proper understanding of the C_{12} - C_{13} phase diagram, the system's potential in delivering compositions suitable as PCMs can be specified. With the main focus on the systems' solid-liquid phase change, which is where the PCMs are defined, the polymorphic phase changes were given a lower priority in this study.

2 Materials and the T-History Method

Using the T-History method, *n*-dodecane ($CH_3(CH_2)_{16}CH_3$), *n*-tridecane ($CH_3(CH_2)_{11}CH_3$) of 99% and 99+% purity (ACROS ORGANICS, n.d.), and the C_{12} - C_{13} blend compositions 5, 10, 15, 17.7, 20, 25, 30, 40, 50, 60, 70, 81, and 90 mol% C_{13} (1.3 mol% expanded uncertainty with a 0.95 confidence) were examined. The blends were prepared by mixing the relevant weights of the pure components in glass test-tubes by rigorous shaking to obtain a single liquid. These were poured into the T-History stainless-steel (SS) test-tubes, in volumes similar to that of the reference. Their weights were between 7.10-7.73 g (0.04 g expanded uncertainty with 0.95 confidence). A solid stainless-steel (SS) reference was used, with the same geometry as the sample test-tubes, and a weight of 144.81 ± 0.04 g. The prepared C_{12} - C_{13} blends and pure components test-tubes, and the reference, after connecting thermocouples and insulating with HT-Armaflex, were kept within an SS containment. This whole set-up (see Figure 1) was then thermally cycled for five cycles in a temperature-programmable climate chamber (ACS Hygros 1200). This heating/cooling cycling was performed at a rate of $0.2 \text{ } ^\circ\text{C min}^{-1}$, between $-29 \text{ } ^\circ\text{C}$ to $+10 \text{ } ^\circ\text{C}$, while maintaining isothermally for 5 hours at each endpoint temperature.

In the T-history method, the unknown thermal properties of a material are found by comparing to a reference with known thermal properties, in sample vessels having the same geometries. The lumped-capacitance conditions need to be met for the T-history evaluation to be valid, by maintaining a Biot number less than 0.1 (Chiu and Martin, 2012; Gunasekara et al., 2016; Gunasekara et al., 2017a). Prior to the polyols' measurements, the T-history set-up was verified with benchmark tests conducted on distilled water, and the alkanes: octadecane, dodecane and tridecane. The distilled-water tests yielded identical temperature profiles, thus verified identical insulations. Whereas, the alkanes tests verified the enthalpy derivations, with the measured fusion enthalpies (with an expanded uncertainty of 10% with 0.95 confidence) consistent with literature.

The stainless steel used in the reference and the SS test-tubes were the type SS316, with a specific heat of $0.5 \text{ kJ kg}^{-1}\text{K}^{-1}$ and a thermal conductivity of $16.2 \text{ W m}^{-1}\text{K}^{-1}$ (AK Steel Corporation, 2007). The temperature measurements were conducted using calibrated T-type thermocouples with an expanded

accuracy of 0.4 °C with 0.95 confidence, logged using a data logger (Keithley 2701). The T-history set-up was verified with benchmark tests conducted using distilled water and octadecane. The distilled water tests verified identical insulations by yielding identical temperature profiles. For octadecane, the measured enthalpies (with an expanded uncertainty of 10% with 0.95 confidence) were consistent with the literature values, hence confirm the validity of the T-History assessments.

3 Results and Discussion

To derive the C_{12} - C_{13} phase diagram, the phase change temperatures of the system were deduced by an overall examination of the temperature, c_p and enthalpy profiles obtained via the T-history measurements. The characteristics obtained during heating and cooling were treated separately, and the Tammann plots were constructed as relevant. This overall evaluation is described here.

3.1 Phase Change Characteristics of the $C_{12}H_{26}$ - $C_{13}H_{28}$ system

The melting and freezing characteristics of the system remained consistent throughout all the five cycles. As examples, the temperature, enthalpy, and c_p profiles of each examined composition for a chosen cycle are summarized in Figure 2, Figure 3 and Figure 4, respectively, for melting (a) and freezing (b). A phase change is: a temperature plateau or a narrow temperature change in the temperature profiles (Figure 2); a sharp enthalpy change in the enthalpy profiles (Figure 3); and a peak in the c_p profiles (Figure 4). To ensure only the real blend's phase change is accounted in the phase diagram, the first complete freezing /melting cycle was excluded in the evaluations. From the remaining four cycles, the three first cycles were chosen for the assessment. The start of a phase change, i.e., the onset was identified by drawing tangents to the leading edge and the baseline of the corresponding c_p peak. Similarly, the end of a phase change, i.e. the offset was chosen at the intersection of tangents on the decreasing edge and the baseline of the c_p peak.

As seen in Figure 2-Figure 4, the pure C_{13} and 90 mol% C_{13} have two distinct phase changes within -29 °C to 10 °C: a polymorphic transformation at lower temperatures, and the melting/freezing at higher temperatures. These characteristics comply with literature, reporting a polymorph on C_{13} (Ventolà et al., 2002; Yan et al., 2013) which gave-rise to solid-solid phase changes in the blends e.g. towards a eutectoid (Ventolà et al., 2002). Certain minor peaks that appeared on a few c_p profiles after melting (e.g. C_{12} melting in Figure 4), but were absent in freezing, were neglected in the evaluation. These could be liquid crystals (c.f. Mettler Toledo, n.d.) or artifacts, but did not influence the overall stability of the system as confirmed by the consistent display of the pure component stable phases.

According to literature, the polymorphic C_{13} is orthorhombic, and it transforms into the rotator phase R_1 prior to melting (Ventolà et al., 2002; Yan et al., 2013). The pure C_{12} is triclinic (T_P) in its stable solid (Ventolà et al., 2002). The T-History results (Figure 2-Figure 4) here indicate that the pure C_{12} and C_{13} melt on average between -11 °C to -9 °C and -7 °C to -4.5 °C, and freeze on-average, within -12 °C to -10.5 °C and -8 °C to -6 °C respectively. The average hysteresis is hence 1-1.5 °C for each pure component,

which is low. Supercooling was negligible, with the maximum observed being 2 °C on the pure C_{12} and 5 mol% C_{13} (e.g. Figure 2 (b)).

The overall c_p peak evolution of the system during melting or freezing indicates a melting/freezing point decrease towards a minimum temperature (Figure 4). This trend agrees with the observations of Ventolà et al. (2002), but contradicts Yilmaz et al. (2009) who observed a reversed scenario, towards a maximum phase change temperature. As shown in Figure 4, two main c_p peaks occurred for the compositions 5-20 mol% C_{13} , except at 17.7 mol% C_{13} , during heating. The low-temperature peak of these two, and the single peak of the 17.7 mol% C_{13} occurred at rather similar temperatures (Figure 4). This, therefore, could be a eutectic peak, as discussed by Ventolà et al. (2002). Strangely, such a secondary peak, however, was absent during freezing in all the compositions, except for the 5 mol% C_{13} . The compositions 25-81 mol% C_{13} had only a single phase change during heating and cooling. Among all evaluated blends, the single phase change peak of the 17.7 mol% C_{13} was the narrowest peak, during both melting and freezing (Figure 4 (a) and (b)) and thus could be the closest to the probable eutectic.

Accounting the selective average phase change trends over the 2nd-4th melting/freezing cycles, the C_{12} - C_{13} heating-based and cooling-based phase diagrams are plotted in Figure 5 (b). To ascertain if the secondary c_p peak identified on the 5-20 mol% C_{13} is indeed of a eutectic, its selective average melting molar enthalpy (Avg,M2-M4-hE,m) is plotted in Figure 5 (a) in a Tammann plot. A eutectic has a characteristic triangular shape in a Tammann plot, where, its enthalpy maximum (peak) occurs at the exact eutectic composition (Rycerz, 2013). The system's solid-state miscibility is also indicated by the Tammann plot where the eutectic enthalpy becomes zero (Rycerz, 2013).

In the phase diagrams in Figure 5 (b), S, L, SSs and SSe respectively denote the solidus, liquidus, and the polymorphic phase change start and the end. The succeeding M or Fr indicate melting or freezing cycles. The liquidus represents: the melting offsets (for 25-100 mol% C_{13}); the probable eutectic offset (for 17.7 mol% C_{13}); or the freezing onsets (for all compositions), respectively. The solidus is made of either the melting onset (for 25-100 mol% C_{13}); the probable eutectic onset (for compositions below 25 mol% C_{13}); or, the freezing offset (for all compositions except 5 mol% C_{13}) respectively. The SSs and SSe are made respectively of the low-temperature and high-temperature inflection points of the polymorphic c_p peaks in heating and cooling. In the Tammann plot (Figure 5 (a)), linear regression was performed on the enthalpies before and after the possible eutectic compositions: 17.7 and 20 mol% C_{13} . These regression plots meet at the exact eutectic composition, here seen just before, but quite close to, the 20 mol% C_{13} . In contrast, the temperature-minimum in the heating-based liquidus exists between 25-30 mol% C_{13} compositions. Therefore, strangely, the composition of the probable eutectic is inconsistent between the Tammann plot and the melting-based liquidus. As during freezing a eutectic indication was absent, that phase diagram cannot be compared against the Tammann plot.

The system definitely has a low-temperature polymorph, attributed by the polymorph of the pure C_{13} . Thus, if this system has a eutectic, it must be in a partially isomorphous system, containing solvus curves to mark partial-miscibility (but cannot be a simple eutectic). However, solid-solid phase changes that can indicate a solvus (e.g. the heneicosane-docosane system (Metivaud et al., 1999) were also absent in any of the compositions, during both heating and cooling. Because of these inconsistencies, it is here decided that the heating-based phase changes cannot be used to conclude on the system's phase diagram. Therefore, the cooling-based phase change trend was selected as a better representation of the final C_{12} - C_{13} phase diagram. This indicates a possible congruent minimum-melting solid solution and polymorphic phases in the C_{12} - C_{13} phase diagram.

3.2 Enthalpy Characteristics of the $C_{12}H_{26}$ - $C_{13}H_{28}$ system

The pure $C_{12}H_{26}$ and $C_{13}H_{28}$ displayed consistent melting and freezing throughout the T-History cycling, as exemplified in Figure 6 and Figure 7 respectively, for the 2nd to 4th cycles. The obtained selective average phase change enthalpies and temperatures agree rather well with those proposed in literature, as Table 2 indicates. (Table 2 neglects the minor variations in C_{12} after melting (c.f. section 3.1), which, if accounted, gives a total melting enthalpy of $232 \pm 23 \text{ kJ kg}^{-1}$, between $-11.4 \pm 0.4 \text{ }^{\circ}\text{C}$ and $-6.9 \pm 0.4 \text{ }^{\circ}\text{C}$).

The selective average enthalpies for melting and freezing of the blend system (excluding the polymorphic changes) are summarized in Table 3.

The total phase change enthalpies of the 90 mol% C_{13} composition and pure C_{13} including the polymorphic changes are $282 \pm 28 \text{ kJ kg}^{-1}$ and $300 \pm 30 \text{ kJ kg}^{-1}$ during heating, and $245 \pm 25 \text{ kJ kg}^{-1}$ and $287 \pm 29 \text{ kJ kg}^{-1}$ during cooling, respectively. The polymorphic C_{13} occurred between $-19.4 \text{ }^{\circ}\text{C}$ to $-18.2 \text{ }^{\circ}\text{C}$ ($\pm 0.4 \text{ }^{\circ}\text{C}$) in heating, and $-19.5 \text{ }^{\circ}\text{C}$ to $-20.3 \text{ }^{\circ}\text{C}$ ($\pm 0.4 \text{ }^{\circ}\text{C}$) in cooling with the enthalpies $66 \pm 6 \text{ kJ kg}^{-1}$ and $46 \pm 6 \text{ kJ kg}^{-1}$, as compared to literature proposing it at $-18 \text{ }^{\circ}\text{C}$ with an enthalpy of 42 kJ kg^{-1} (Mondieig et al., 2004). From the blends evaluated, the minimum-melting composition in the system lies at 17.7 mol% C_{13} . This composition melts between $-15.7 \text{ }^{\circ}\text{C}$ to $-12.4 \text{ }^{\circ}\text{C}$ ($\pm 0.4 \text{ }^{\circ}\text{C}$) with an enthalpy of $185 \pm 18 \text{ kJ kg}^{-1}$, and freezes around $-15 \text{ }^{\circ}\text{C}$ to $-16.4 \text{ }^{\circ}\text{C}$ ($\pm 0.4 \text{ }^{\circ}\text{C}$) with an enthalpy of $165 \pm 16 \text{ kJ kg}^{-1}$. The 5 mol% C_{13} composition has the maximum enthalpy in melting and freezing (within the evaluated compositions), on average $277 \pm 28 \text{ kJ kg}^{-1}$ and $248 \pm 25 \text{ kJ kg}^{-1}$ respectively.

3.3 Experimental Phase Diagram of the $C_{12}H_{26}$ - $C_{13}H_{28}$ system

The experimental results presented here have captured the complexity in deriving the phase diagram based on either the cooling or heating cycles. The phase change during heating was complex and contradicting, as the systems displays a probable eutectic which is not possible when the system at the same time contains polymorphs at lower temperatures, and the needed solvus is absent. Based on this,

the phase diagram of the C_{12} - C_{13} system is proposed using the selective average phase change temperatures during cooling, in Figure 8. There, S, L, SSe and SSs indicate the solidus, liquidus, and the solid-solid phase change start and the end. The onsets and offset choices are as described in section 3.1. In this proposed phase diagram (Figure 8, see phase diagram data in supplementary data), the liquidus decreasing towards a temperature minimum and the polymorphic phases of the C_{12} - C_{13} system, agree rather well with the observations of Ventolà et al. (2002), though, completely contradicts those of Yilmaz et al. (2009).

However, the thermal properties here which indicated: the absence of a eutectic phase change during cooling; the lack of solvus curves to indicate a partial-miscibility in either cooling or heating; and the obvious occurrence of low-temperature polymorphic phases, altogether fail to attest that the temperature minimum in the C_{12} - C_{13} system is a eutectic. In contrast, the C_{12} - C_{13} system appears to deliver a phase diagram, as in Figure 8, with a congruent minimum-melting solid solution, and polymorphic phases at lower temperatures. If this is verified, the C_{12} - C_{13} system contains a blend composition even better than a eutectic as a PCM (Gunasekara et al., 2017b). Therefore, the phase diagram identified for the C_{12} - C_{13} system in the present work contradicts the phase diagrams proposed by both Ventolà et al. (2002) and Yilmaz et al. (2009).

Interestingly, Ventolà et al. (2002) presented that the 30 and 50 mol% C_{13} compositions melt from the R_i phase, similar to C_{13} , and the C_{12} - C_{13} phase diagram with a partially isomorphous eutectic between the T_p and R_i phases. However, their solvus curves were presented in dotted lines, without explaining the reasons (section 1). Without knowing these reasons and their detailed evaluation methodology, the discrepancy between Ventolà et al. (2002) and the present investigation failing to corroborate such a eutectic because a solvus is absent, cannot be explained. Generally, a completely miscible (i.e. a continuous) solid solution occurs between components with similar crystal structures (He et al., 2003), although, violations of this rule also exist (e.g. the C_{14} - C_{16} alkanes system (Mondieig et al., 2004)). Therefore, the R_i structure Ventolà et al. (2002) identified for the blends either, is an exceptional case of a continuous solid solution with the same structure of the melting phase of C_{13} , or implies a complex phase change in the system that masks the partial miscibility. It could also be that either the continuous solid solution identified herein, or the eutectic of Ventolà et al. (2002) is a metastable phase, which will revert to a eutectic or a continuous solid solution, respectively, with time. However, if this eutectic is the stable phase, then it must be accompanied by a stable solvus.

To understand these complexities and to confirm the proposed phase diagram, extensive crystallographic and microstructural assessment of most of the C_{12} - C_{13} compositions (within 5-90 mol% C_{13}) are vital. These could be coupled with e.g. cycling tests, and chemical property assessments. Thereby, e.g. the reasons why a possible eutectic phase change in cooling and/or a solvus was absent could be explained. Interestingly, a behavior of an opposite nature was identified e.g. on a pure alkanol: hexadecanol, which displayed a single DSC c_p peak during heating, but two distinct peaks in cooling (Métivaud et al., 2005). For hexadecanol, this was explained as a solid-solid phase change peak that overlapped with melting during heating (Métivaud et al., 2005). Identifying if similar overlapping masked

the eutectic in cooling and solvus indications in both heating and cooling in the C_{12} - C_{13} system also requires extensive physicochemical assessments.

Another aspect of PCM-design interest worth detailed investigations, is the system's susceptibility to metastability. This could be evaluated by plotting kinetic phase diagrams (i.e., non-equilibrium phase diagrams) of the system for different heating/cooling rates. That could verify whether the R_1 phase identified on the 30 and 50 mol% C_{13} Ventolà et al. (2002) is stable or metastable, and perhaps even shed understanding on the completely different phase change trend Yilmaz et al. (2009) experienced.

The potentially congruent minimum-melting point in the C_{12} - C_{13} system identified in the present study, exists between around 15-20 mol% C_{13} , freezing and melting around -17 °C to -15 °C, and -16 °C to -12 °C, with the respective enthalpies 187-192 kJ kg⁻¹ and 220-222 kJ kg⁻¹. The 17.7 mol% C_{13} exhibited the narrowest phase change, melting and freezing between around -15.7 °C to -12.4 °C and -15 °C to -16.4 °C, with the enthalpies 185 kJ kg⁻¹ and 165 kJ kg⁻¹ respectively. This composition undergoes no supercooling, and only minor hysteresis of around 1-3 °C. Therefore, the 17.7 mol% C_{13} composition appears potentially attractive as a PCM for e.g. freezing refrigeration applications. Cycling tests, thermal conductivity evaluation and extensive thermal and physicochemical property assessments of the system should complement the results here, to confirm its PCM-suitability. If the polymorphic phase changes in the system would lead to a eutectoid as Ventolà et al. (2002) found, this could be suitable as a solid-solid PCM, once its TES design properties are established.

4 Conclusions

The T-History evaluations imply a potential congruent minimum-melting solid solution in the $C_{12}H_{26}$ - $C_{13}H_{28}$ system, succeeded by polymorphic changes. This however, contradicts the results on the system in literature, presenting a partially isomorphous eutectic and a eutectoid, or with a maximum-melting liquidus, respectively. In the present investigation, only during heating, for some compositions a secondary phase change c_p peak implied a probable eutectic between the compositions 25-30 mol% C_{13} . However, in a Tammann plot of this probable eutectic, the eutectic composition in-contrast lied at a composition between 17.7-20 mol% C_{13} . In addition, neither in cooling nor heating, any solid-solid phase change occurred that could indicate a solvus in the system. Therefore, as a whole, the cooling-based phase change trends gave rise to a more correct phase diagram. Whereas, the behavior observed during heating is inconsistent, which implied a eutectic which however cannot exist without solvus curves in this system with polymorphs. Hence, the final phase diagram of the system was chosen only to represent the cooling-based behavior, which indicates a congruent minimum-melting solid solution and a polymorphic change.

The minimum-melting composition in the system lies closest to the 17.7 mol% C_{13} from the evaluated compositions. The 17.7 mol% C_{13} composition melts and freezes at -16 °C to -12 °C and -17 °C to -15 °C, with the respective enthalpies 185 kJ kg⁻¹ and 165 kJ kg⁻¹, no supercooling and only minor hysteresis (1-3 °C). Hence, it appears attractive as a potential PCM in freezing refrigeration applications. Comprehensive thermal and physicochemical property evaluations of the $C_{12}H_{26}$ - $C_{13}H_{28}$ system are also necessary to explain its phase change differences observed during heating and cooling, and thereby to confirm the phase diagram.

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Figure 1. The T-history set-up (Left: photograph inside the SS containment, Right: a schematic)

Figure 2. The melting (M) and freezing (Fr) temperature profiles of the evaluated C_{12} - C_{13} compositions for chosen cycles (2-4) (shown by 100 min intervals for illustrative clarity)

Figure 3. The melting (M) and freezing (Fr) enthalpy profiles of the evaluated C_{12} - C_{13} compositions for chosen cycles (2-4) (shown by 100 kJ kg⁻¹ intervals for illustrative clarity)

Figure 4. The melting (M) and freezing (Fr) c_p profiles of the evaluated C_{12} - C_{13} compositions for chosen cycles (2-4) (shown by 50 kJ kg⁻¹K⁻¹ intervals for illustrative clarity)

Figure 5. The comparison of the C_{12} - C_{13} system's (a) Tammann plot for the probable eutectic during heating, with (b) the phase diagrams during freezing and melting. (The expanded uncertainties with 0.95 confidence for enthalpy, composition and temperature are: 10%, 0.013, and 0.4 °C respectively)

Figure 6. The (a) melting (M), and (b) freezing (Fr), enthalpy profiles of pure $C_{12}H_{26}$ over the 2nd-4th cycles (the dotted lines mark the considered temperature range of phase change)

Figure 7. The (a) melting (M), and (b) freezing (Fr), enthalpy profiles of pure $C_{13}H_{28}$ over the 2nd-4th cycles (the dotted lines mark the considered temperature ranges of phase changes)

Figure 8. The proposed phase diagram for the dodecane-tridecane binary system (temperature and molar composition expanded uncertainties with 0.95 confidence are 0.4 °C and 1.3 mol%)

Table 1. The thermal and crystallographic characteristics of dodecane and tridecane, from literature

Parameter	Dodecane (C ₁₂ H ₂₆)	Tridecane (C ₁₃ H ₂₈)
Fusion/Melting temperature (°C)	-10 (Ventolà et al., 2002; Mondieig et al., 2004) / -9.6 (Yilmaz et al., 2009; Jankowski and McCluskey, 2014)	-5.5 (Ventolà et al., 2002; Mondieig et al., 2004; Jankowski and McCluskey, 2014)/ -4, -6 (Yilmaz et al., 2009)
Fusion enthalpy (kJ kg⁻¹)	210 (Ventolà et al., 2002; Mondieig et al., 2004)/ 216 (Yilmaz et al., 2009; Jankowski and McCluskey, 2014)	157 (Ventolà et al., 2002; Mondieig et al., 2004; Yilmaz et al., 2009) / 196 (Jankowski and McCluskey, 2014)
Melting phase	T _p (Ventolà et al., 2002; Mondieig et al., 2004)	R _i (Ventolà et al., 2002; Mondieig et al., 2004)

Table 2. The comparison of the pure components' obtained thermal properties with literature^a (avg: average)

Material	Fusion Temp. (°C)	Melting/Freezing Temp. (°C) ^b	Fusion enthalpy (kJ kg ⁻¹)	Melting/Freezing enthalpy (kJ kg ⁻¹) ^c
	Literature	This work (avg.)	Literature	This work (avg.)
C ₁₂ H ₂₆	-10 (Ventolà et al., 2002; Mondieig et al., 2004), -9.6 (Yilmaz et al., 2009; Jankowski and McCluskey, 2014)	-11.4 to -8.8/ -10.5 to -11.6	210 (Ventolà et al., 2002; Mondieig et al., 2004), 216 (Yilmaz et al., 2009; Jankowski and McCluskey, 2014)	216/ 230
C ₁₃ H ₂₈	-5.5 (Ventolà et al., 2002; Mondieig et al., 2004; Jankowski and McCluskey, 2014), -4, -6 (Yilmaz et al., 2009)	-6.7 to -4.5/ -6.3 to -7.9	157 (Ventolà et al., 2002; Mondieig et al., 2004; Yilmaz et al., 2009), 196 (Jankowski and McCluskey, 2014)	182/ 208

^athe experimental pressure was not controlled in the study, beyond the typical atmospheric pressure (101±2 kPa)

^{b,c}with expanded uncertainties at a 0.95 confidence, of ^b0.4 °C and ^c10%

Table 3. The average melting and freezing enthalpies of the evaluated C_{12} - C_{13} compositions^a

Composition (mol% C_{13}) ^b	Average melting enthalpy (kJ kg ⁻¹) ^c	Average freezing enthalpy (kJ kg ⁻¹) ^c
0	232	230
5	277	248
10	256	220
15	222	187
17.7	185	165
20	220	192
25	197	177
30	186	147
40	174	148
50	168	150
60	192	169
70	191	189
81	177	161
90	169.5	183.5
100	182	208

^athe experimental pressure was not controlled in the study, beyond the typical atmospheric pressure (101±2 kPa)^{b,c}with expanded uncertainties at a 0.95 confidence, of ^b1.3 mol% and ^c10%

Supplementary Data

Table 4. The phase diagram data of the proposed $C_{12}H_{26}$ - $C_{13}H_{28}$ phase diagram^a (selective average of 2nd-4th cooling cycles). Here, the pure C_{12} and C_{13} freeze into T_p and R_l phases respectively, while $S_{C_{12},C_{13}}$ is their solid solution phase (crystallography is unknown). The polymorphic phase is considered as orthorhombic, denoted with O. L is the liquid, and t is the temperature in °C, where the subscripts SS, S and L denote the solid-solid phase change, the solidus, and the liquidus. Here, na: not available, and u:unknown.

Mole fraction, $X_{C_{13}}$ ^b	tSS, onset (°C)	tSS, offset (°C)	Phases	tS, (°C)	tLiq (°C)	Phases
0	na	na	na	-10.5	-10.5	T_p
0.05	u	u	u	-16.7	-13.0	$S_{C_{12},C_{13}} + L$
0.1	u	u	u	-17.0	-15.0	$S_{C_{12},C_{13}} + L$
0.15	u	u	u	-17.0	-15.3	$S_{C_{12},C_{13}} + L$
0.177	u	u	u	-16.4	-15.1	$S_{C_{12},C_{13}} + L$
0.2	u	u	u	-17.1	-15.0	$S_{C_{12},C_{13}} + L$
0.25	u	u	u	-16.3	-14.8	$S_{C_{12},C_{13}} + L$
0.3	u	u	u	-15.7	-14.1	$S_{C_{12},C_{13}} + L$
0.4	u	u	u	-15.2	-13.4	$S_{C_{12},C_{13}} + L$
0.5	u	u	u	-15.2	-12.3	$S_{C_{12},C_{13}} + L$
0.6	u	u	u	-13.8	-11.1	$S_{C_{12},C_{13}} + L$
0.7	u	u	u	-13.1	-9.9	$S_{C_{12},C_{13}} + L$
0.81	u	u	u	-10.8	-8.9	$S_{C_{12},C_{13}} + L$
0.9	-24.9	-24.0	O + $S_{C_{12},C_{13}}$	-9.1	-7.5	$S_{C_{12},C_{13}} + L$
1	-19.5	-19.5	O	-6.3	-6.3	R_l

^aThe experimental pressure was not controlled in the study, beyond the typical atmospheric pressure 101±2 kPa^{b,c}The expanded uncertainties, of molar composition and temperature, with a 0.95 level of confidence, are ^b1.3% and ^c0.4 °C respectively

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figures- Greyscale

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Figure 14.

Figure 15.

Figure 16.

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