Phase Change Materials Emulsions for heat transfer and storage applications

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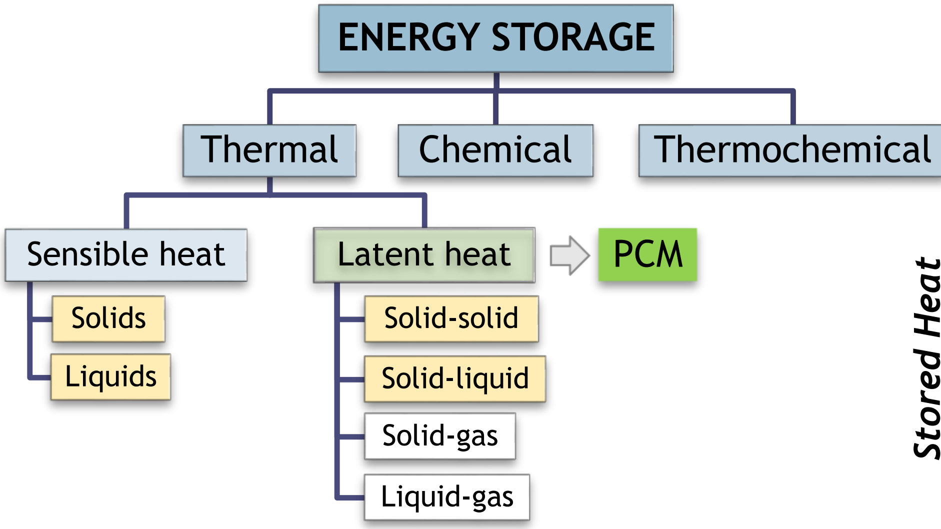
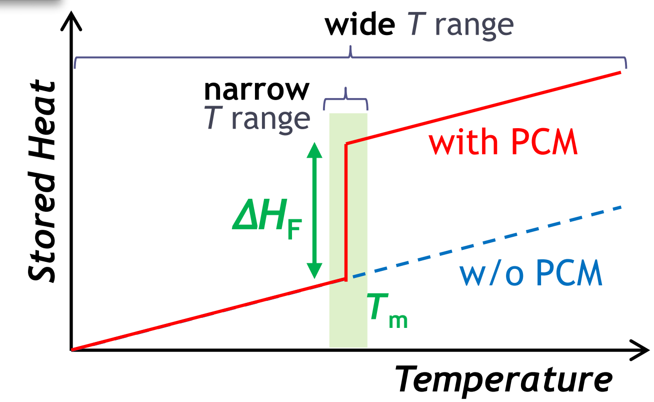
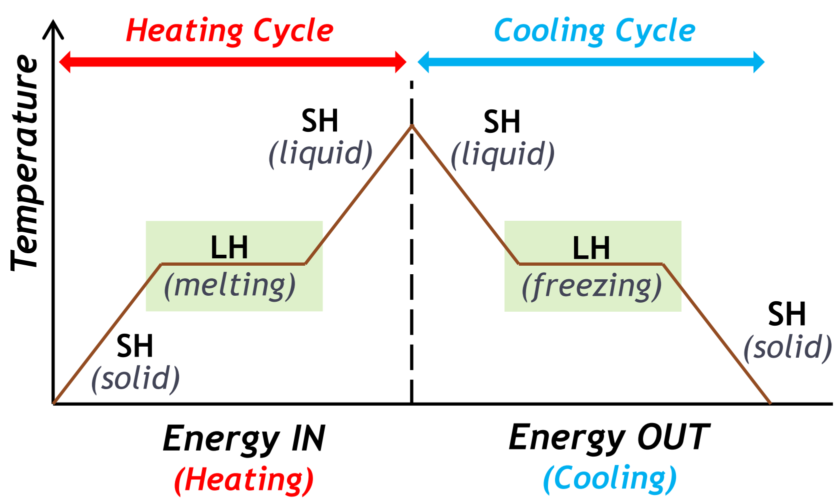
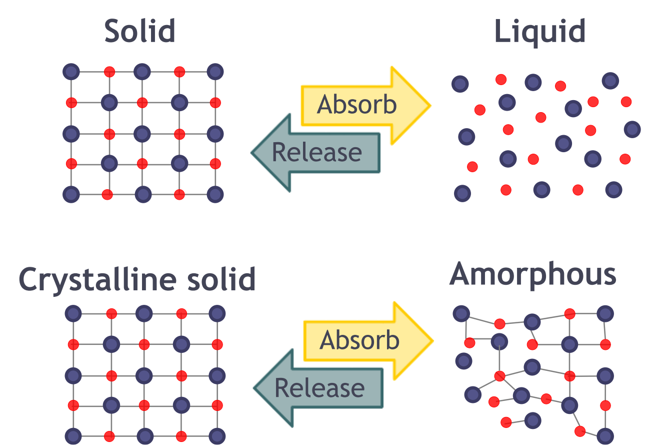
Padova, 22nd May 2019

- THERMAL ENERGY STORAGE

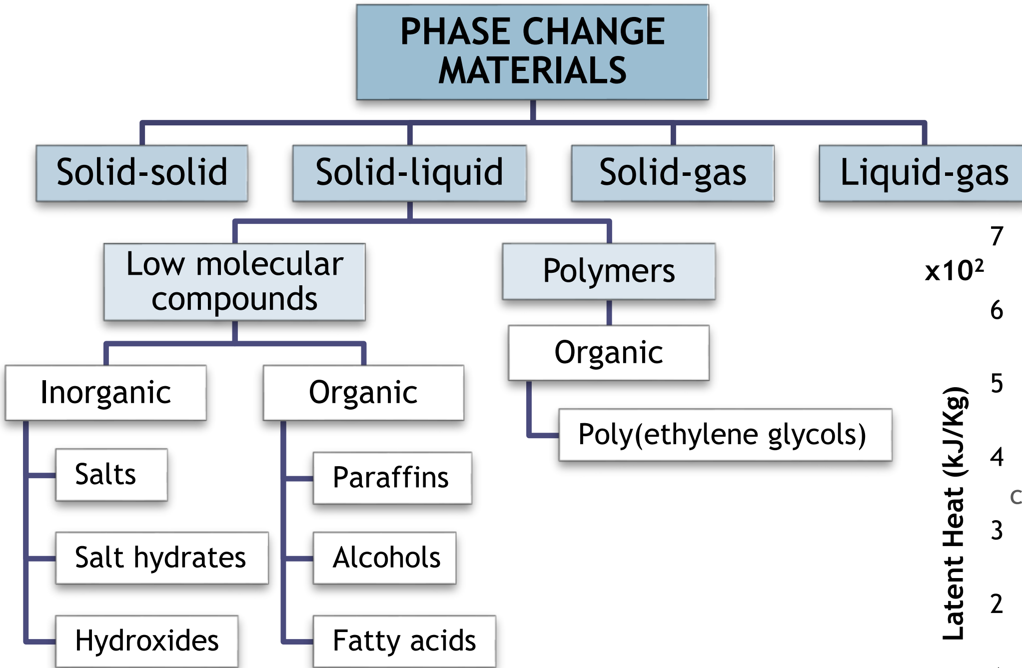


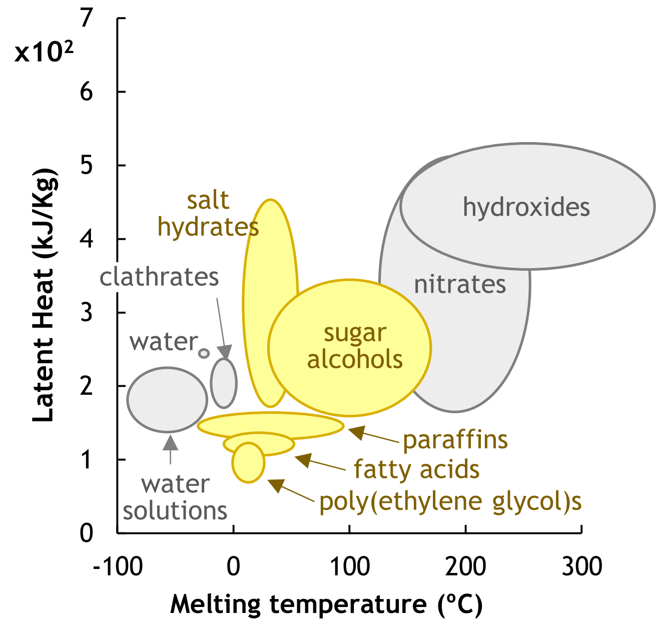






BACKGROUND





Cabeza et al. *Renew. Sust. Energ. Rev.* 15 (2011) 1675-1695.

- PCM REQUIREMENTS

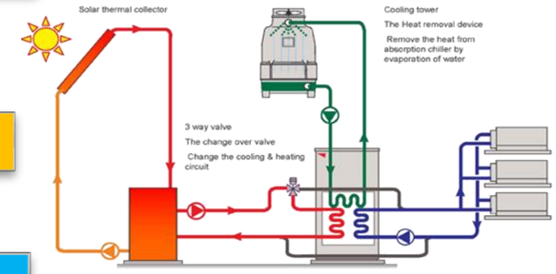
- **Freeze** and **melt** at a **desired temperature**.
- **Freeze** and **melt** in a **narrow temperature** range.
- **Similar melting** and **freezing** points.
- **High latent heats**.
- **High thermal conductivity**.

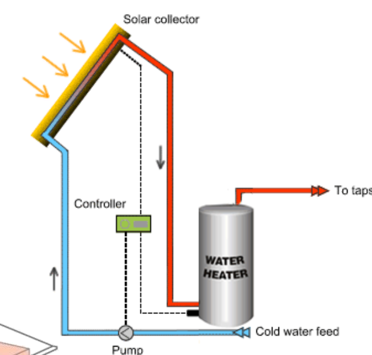
BACKGROUND

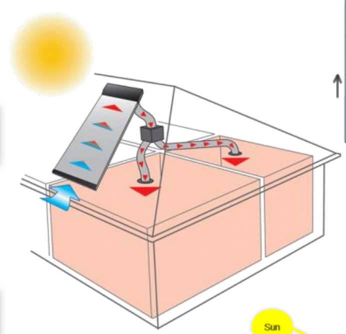
- POTENTIAL PCM APPLICATIONS

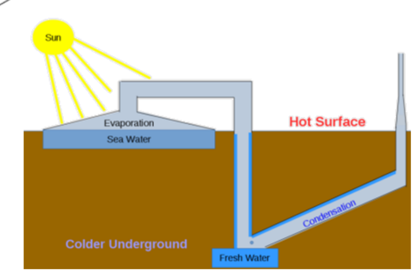
POTENTIAL PCMs FOR TES*

- LOW TEMPERATURE (-20°C to 5°C)
  - Domestic refrigerator
  - Commercial refrigerated products
- MEDIUM-LOW TEMPERATURE (5°C to 40°C)
  - Free cooling
  - Building passive heating/cooling
  - Solar absorption chiller
  - Evaporative and radiative cooling
  - Air conditioning system
- MEDIUM TEMPERATURE (40°C to 80°C)
  - Solar air heaters
  - Solar stills
  - Solar domestic hot water
  - Electric devices
- HIGH TEMPERATURE (80°C to 200°C)
  - Solar absorption cooling
  - On-site/off-site waste heat recovery
  - Solar thermal electricity generation









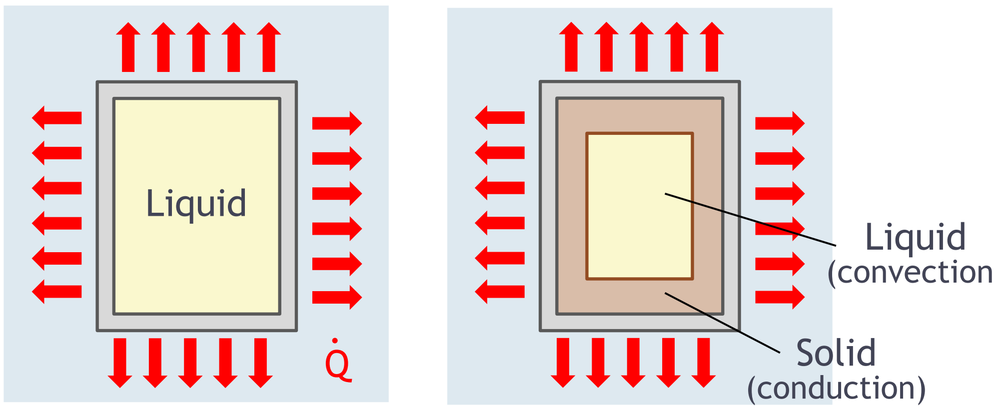
*Du et al. *Appl. Energy*. 220 (2018) 242-273.

BACKGROUND

✘ PROBLEMS *(using PCMs in Thermal Energy Storage systems)*

- Phase separation.
- Tendency for super-cooling.
- Low heat transfer rate.

↳ long charging and discharging processes.



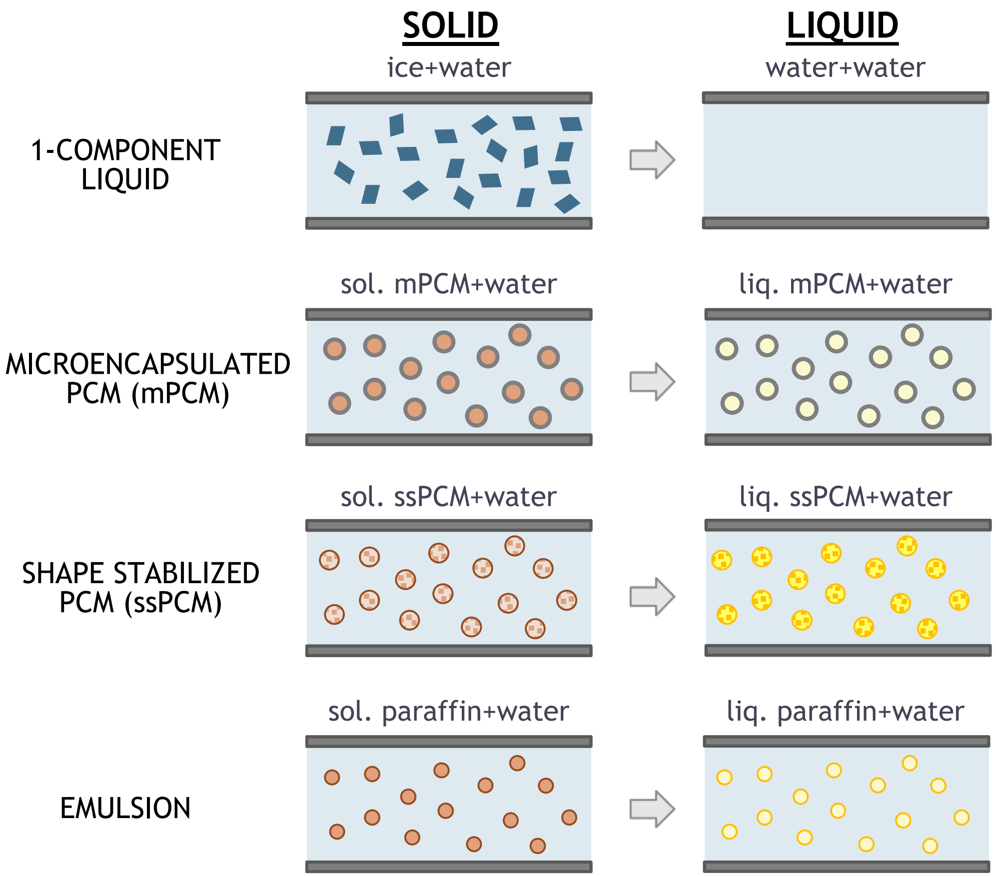
- SOLUTIONS *(to reduce thermal resistance of PCM-Heat Transfer Fluid boundary)*

- **HEAT TRANSFER ENHANCEMENT**
  - STATIC PCMs
    - TRADITIONAL ⇨ extending heat transfer surface.
    - High conductive additives ⇨ **nano-PCMs** or **NePCMs**.
  - TRANSPORTABLE PCMs
    - Indirect-contact ⇨ intermediate PCM-HTF separation, PCM is agitated (**dynamic PCM**).
    - Direct-contact
      - Direct-contact PCM system
      - Direct-contact HTF system

      ⇩ no PCM-HTF separation

DIRECT-CONTACT. HTF SYSTEMS

- PCM is circulating with the HTF (**slurries**).



✘ Encapsulation → ↑ cost
↑ thermal resistance

✘ Can present destabilization problems.

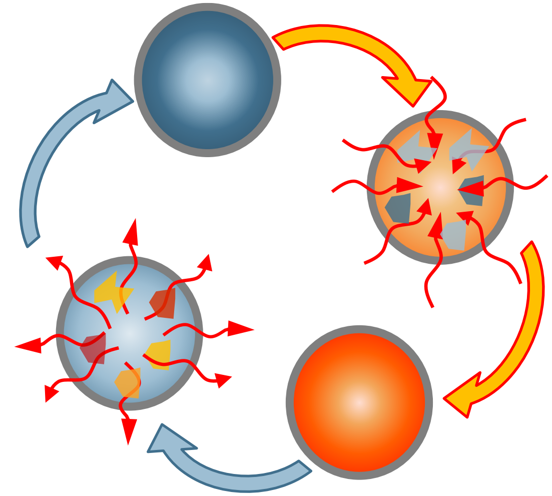
✘ To **avoid thickening issues** ⇨ PCM content **<20-30 wt.%**
⇨ Low energy storage capacity.

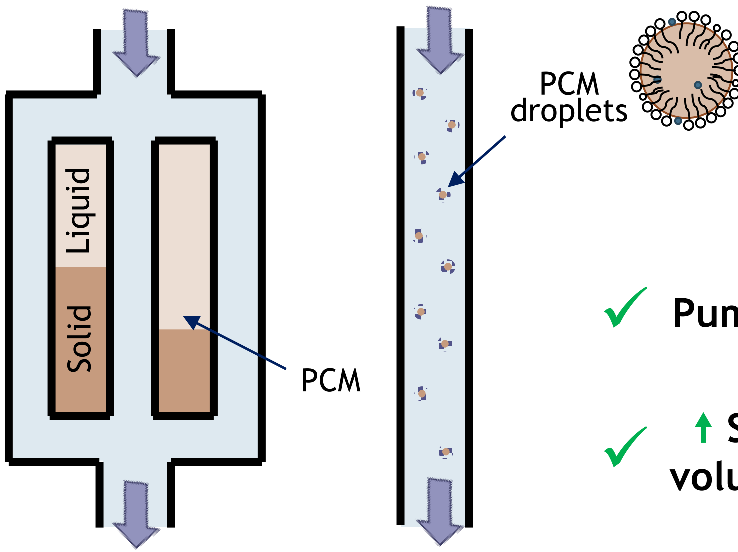
C14(35 wt%)/W
(brij 30)

CEC-500-2006-026.

- PHASE CHANGE MATERIAL EMULSIONS

- **Phase Change Material Emulsions (PCMEs):** latent heat storage fluids consisting in dispersions of fine PCM droplets in carrier fluids





✓ **Pumpable** ⇨ Same medium to transport/store energy

✓ ↑ **Surface/ volume ratio** ⇨ ↑ Heat transfer rate of stored energy

✗ ↑ **Viscosity** ⇨ ↑ **Pumping power**

✓ ↑ **Heat capacity** ⇨ Possibility of ↓ mass flow ⇨ ↓ **Pumping power**

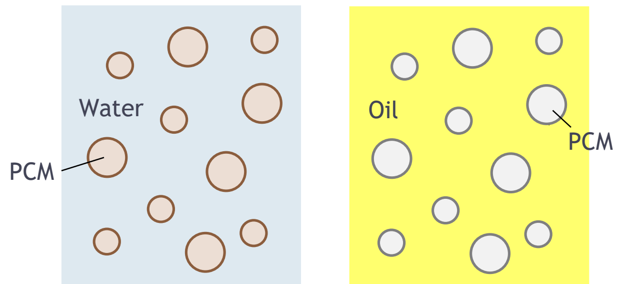
✗ ↑ **Instability problems**

✗ ↑ **Sub-cooling**

- EMULSION TYPES

- Depending on the **configuration:**

PCM EMULSIONS



PCM-in-Water (PCM/W)   PCM-in-Oil (PCM/Oil)

- Selecting immiscible PCM-carrier fluid combinations is possible to prepare:
  - **PCM/Water** emulsions
  - **PCM/Oil** emulsions

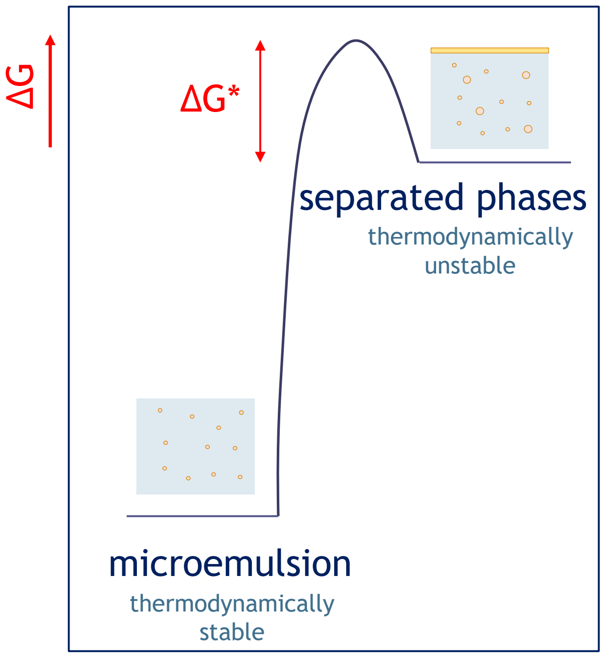
- **PCM/Oil** usually exhibit **higher viscosities** than PCM/W but can **operate** within a **wider temperature range**.

- Depending on the **droplet size:**
  - **Macroemulsions**: sizes > 1 μm
  - **Microemulsions:** sizes from 100 nm to 1 μm
  - **Nanoemulsions** (**miniemulsions**): sizes ~100 nm.

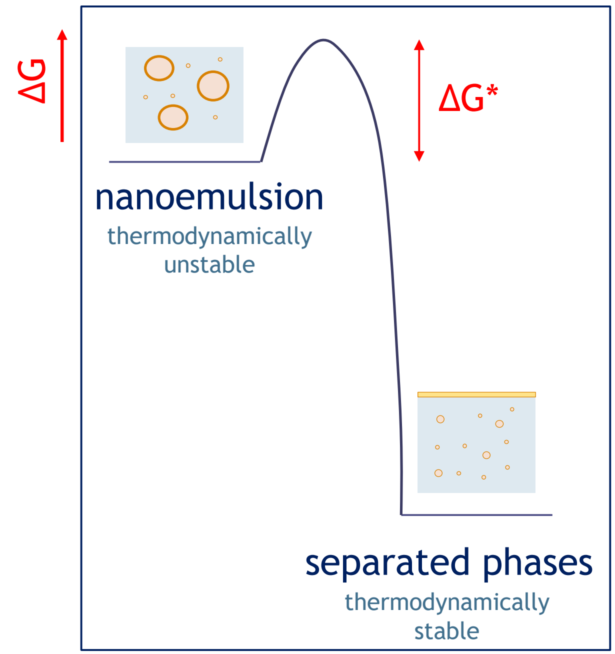
↳ Discrepancies about the limit between micro- and nano-.

BACKGROUND

MICROEMULSION FORMATION



NANOEMULSION FORMATION



Mc Clements *Soft Matter* 8 (2012) 1719.

- ✓ **Thermodynamically stable** (spontaneous formation).
- ✗ **Destabilized** by **composition** and **temperature changes**.
- ✗ Sizes ~**µm.**
- ✗ High surfactant content.

- ✗ **Thermodynamically unstable** (formed intentionally).
- ✓ Very low destabilization kinetics (**kinetically stable**).
- ✓ Sizes lower than ~**300 nm.**
- ✓ Low surfactant content.

PCMEs FORMULATION

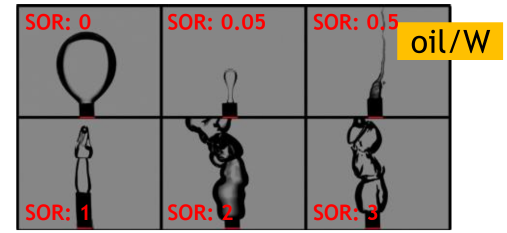
- FORMULATION PARAMETERS

- **FORMULATION PARAMETERS**
  - Surfactant
    - Type/nature
    - Surfactant-to-oil ratio (SOR)
    - Cosurfactant, HLB
  - Dispersed Phase
    - Type/nature
    - Viscosity
  - Continuous Phase
    - Type/nature
    - Viscosity
  - Preparation Method
    - Low-energy
    - High-energy

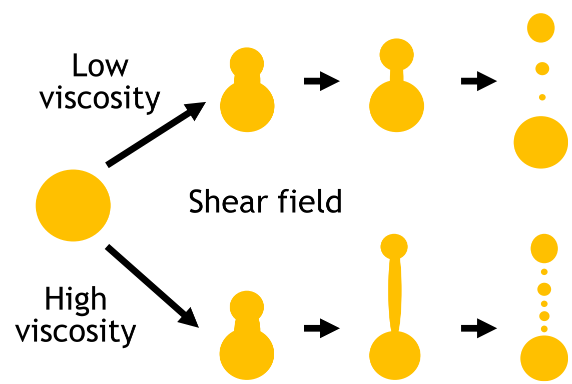
Viscosity (Dispersed Phase) + Viscosity (Continuous Phase) → Continuous/disperse phase Viscosity ratio

(particularly important when emulsification occurs in a shear field under laminar conditions)

Droplet shape analysis obtained at different SOR

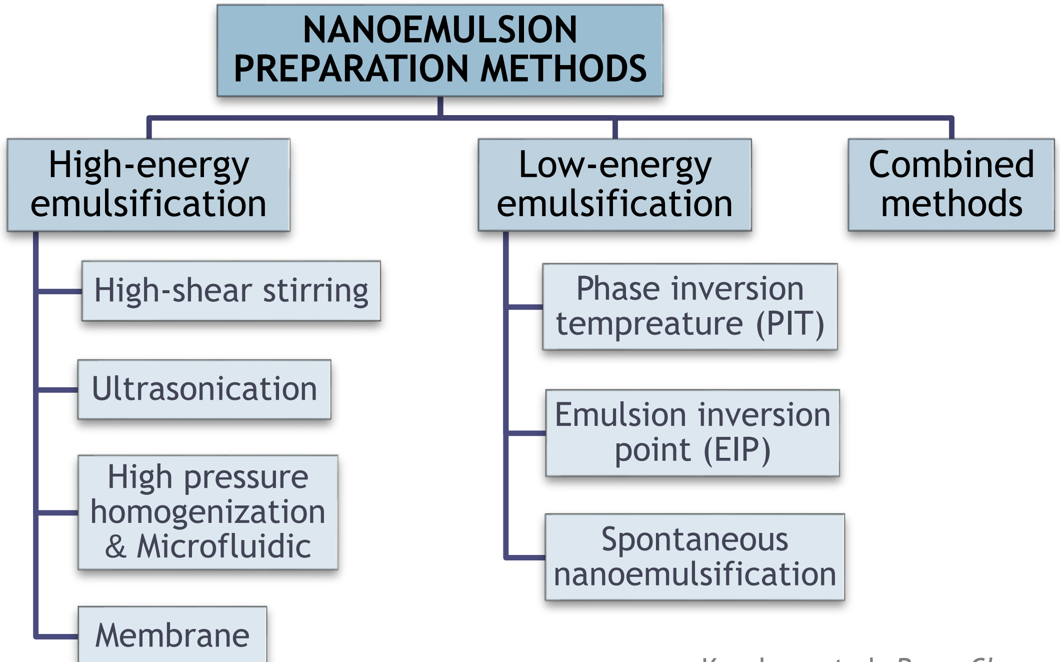


Komaiko et al. *J. Food Lipids* 146 (2015) 122-128.



S. Tcholakova et al. *J. Colloid Interface Sci.* 310 (2007) 570–589.

- PREPARATION METHODS

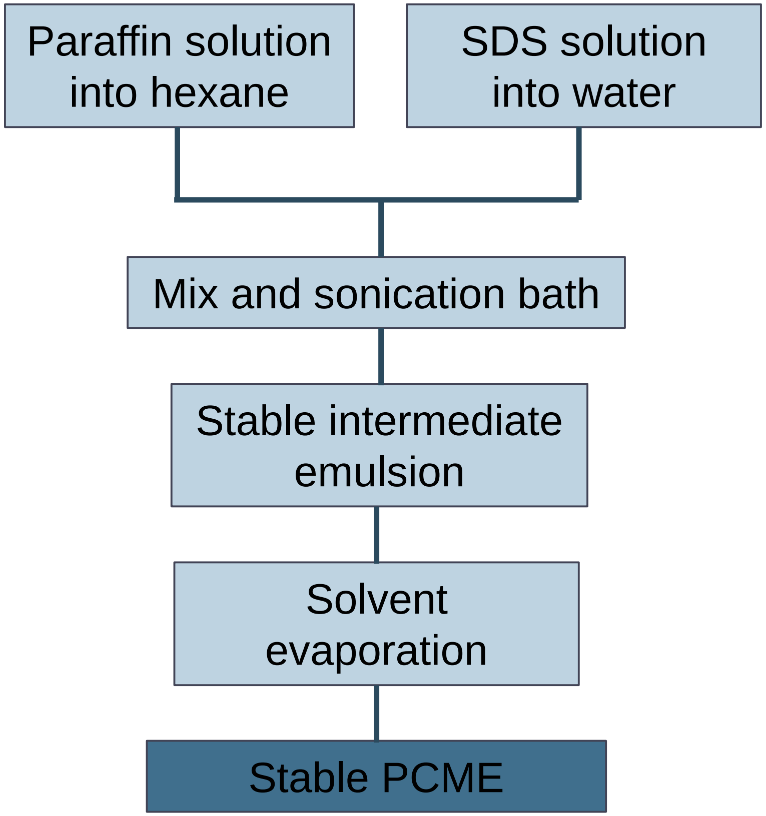


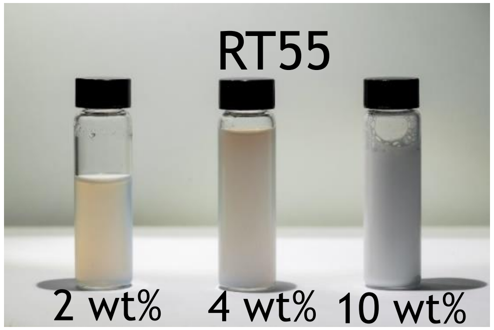
Koroleva et al. *Russ. Chem. Rev.* 81 (2012) 21-43.

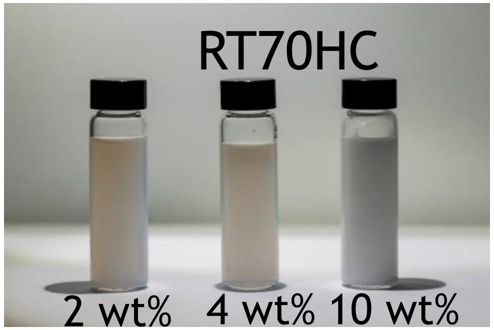
- **HIGH-ENERGY METHODS:** emulsification based on **selected composition** and **supplied energy**. *Power density ~ 10^8-10^{10} W/kg*
- **LOW-ENERGY METHODS:** nanoemulsions are produced as a result of a **phase transition/inversion** during emulsification. *Power density ~ 10^3-10^5 W/kg*
- **COMBINED METHODS:** combination of high- and low-energy emulsifications.

PCMEs FORMULATION

- Solvent-assisted emulsification of paraffin







Agresti, Fedele, Rossi, Cabaleiro, Bobbo, Ischia, Barison.
Solar Energy Materials and Solar Cells (2019)194, 268-275.

Average hydrodynamic size and ζ-potential of suspensions

Sample	average size (nm)	ζ-potential (mV)
RT55 2 wt%	91	-104
RT55 4 wt%	83	-74
RT55 10 wt%	177	-68
RT70HC 2 wt%	65	-67
RT70HC 4 wt%	110	-57
RT70HC 10 wt%	223	-46

PCMEs PROPERTIES

- STORAGE CAPACITY

- Total **storage capacity** of PCMEs is the sum of sensible and latent heat capacities.

$$\text{Storage Capacity} = \underbrace{\int_{T_i}^{T_f} \rho \cdot c_p \cdot dT}_{\text{Sensible heat}} + \underbrace{\bar{\rho} \cdot \Delta h}_{\text{Latent heat}}$$

- Phase change temperatures (T_m, T_{cr})
- Latent heat (Δh)
- Isobaric heat capacity (c_p)
- Density (ρ)

- HEAT TRANSFER CAPABILITY

- PCMEs should **rapidly transfer stored heat** with **low pumping powers**.

$$\text{Heat Transfer Capability} = \frac{\rho^a \cdot k^b \cdot c_p{}^c}{\mu^d}$$

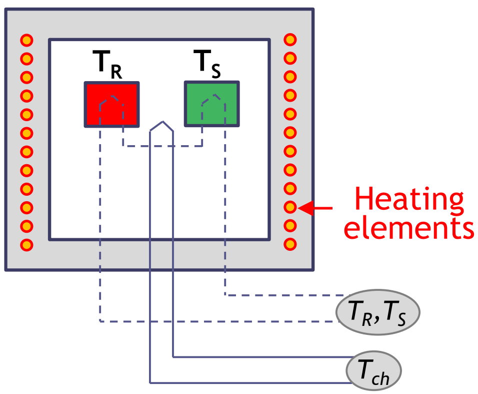
$$\text{Pumping power} = f(\mu, \rho, c_p, k)$$

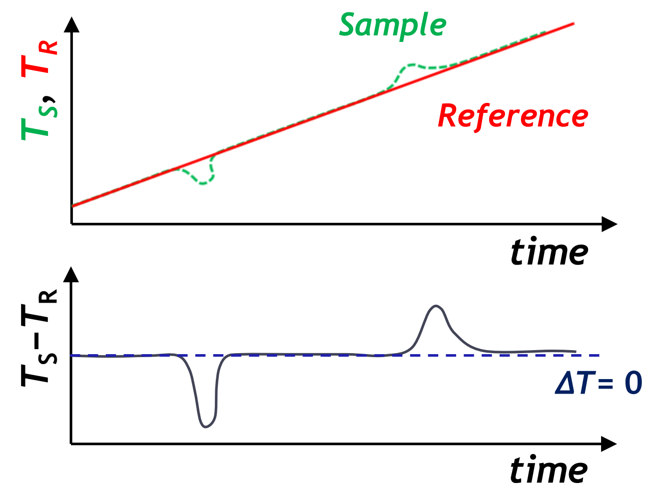
- Thermal conductivity (k)
- Dynamic viscosity (μ)
- Isobaric heat capacity (c_p)*
- Density (ρ)

* For PCMEs undergoing phase change, c_p would be the apparent heat capacity

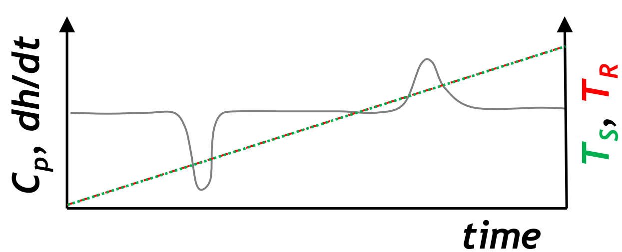
- PHASE CHANGE CHARACTERIZATION

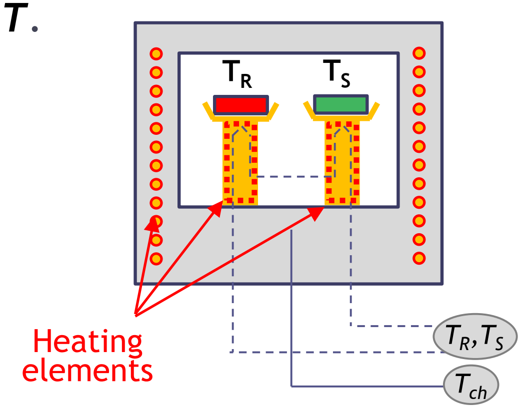
- **DIFFERENTIAL THERMAL ANALISIS (DTA):** studies the **temperature difference** between reference and sample when heated/cooled with the same heat flux.





- **DIFFERENTIAL SCANNING CALORIMETRY (DSC):** measures the amounts of **heat** that must be provided to sample and reference cells in order to obtain **in both cells the same *T***.

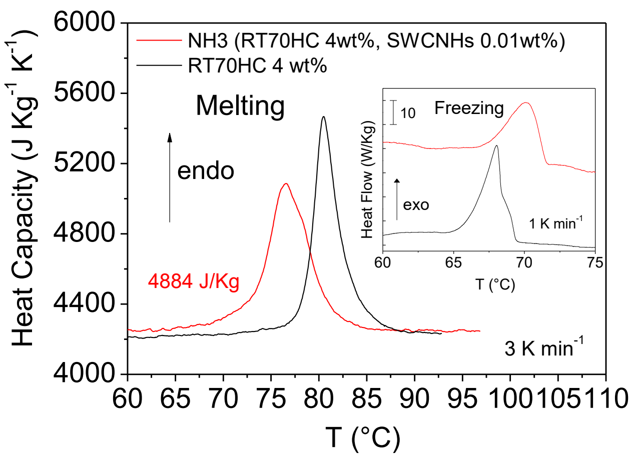




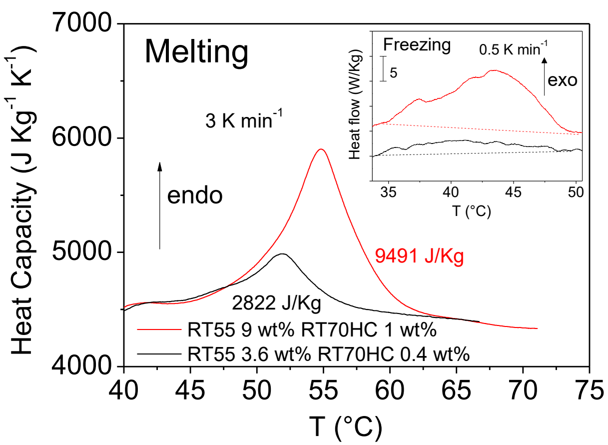
- NUCLEATING AGENT

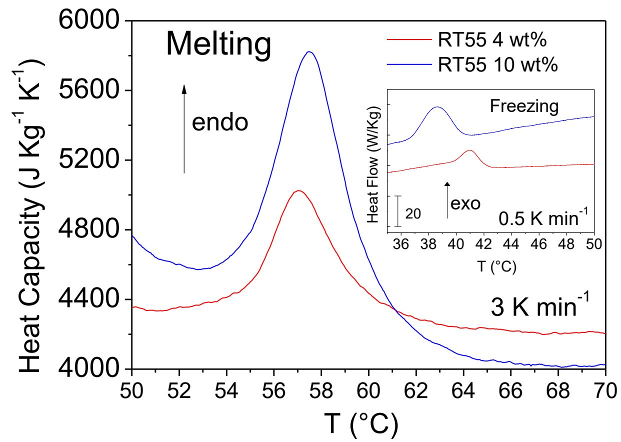
- **NUCLEATING AGENTs:** substances (usually impurities) with a low phase tension that **act as seeds to start nucleation**. Inside PCM or at PCM-carrier fluid surface.

- **TYPES:**
  - **Nanoparticles:** metallic, metal oxides, carbon nanostructures, etc.
  - **PCM** with **higher melting** temperature.



Agresti, Fedele, Rossi, Cabaleiro, Bobbo, Ischia, Barison. *Solar Energy Materials and Solar Cells (2019)194, 268-275.*

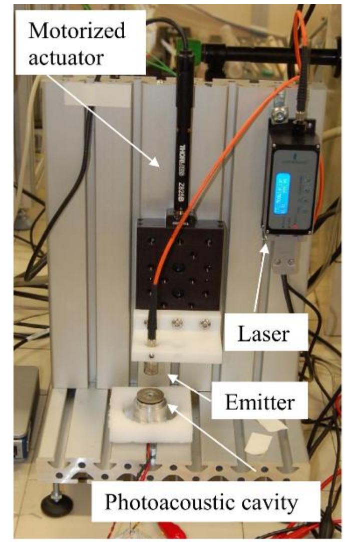




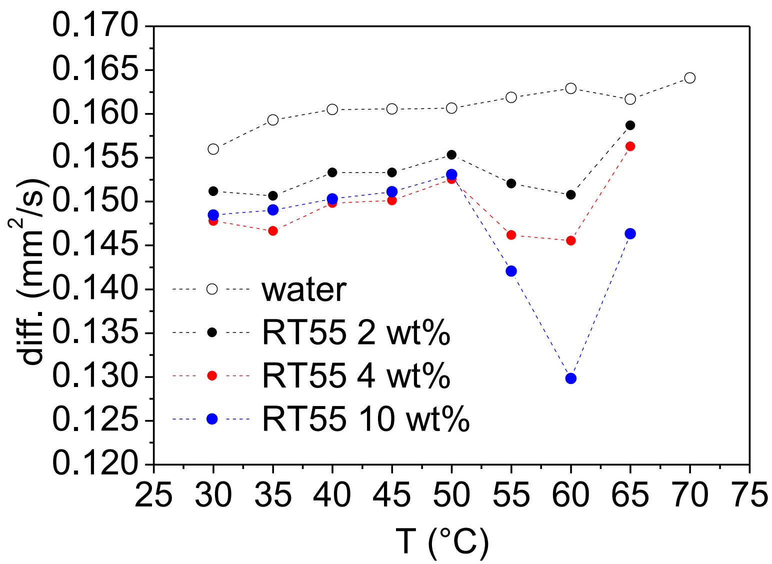
PCMEs PROPERTIES

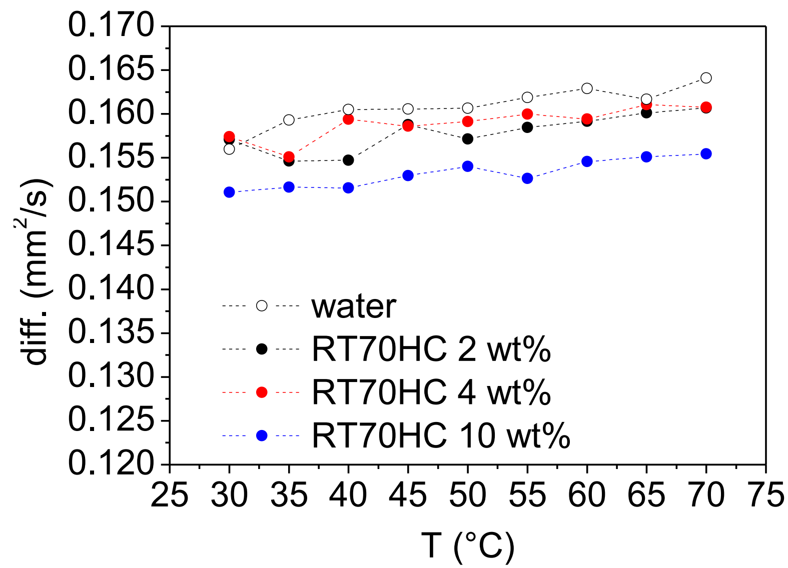
- THERMAL CONDUCTIVITY

- Most organic PCMs exhibit low k → **PCM emulsions** are expected to exhibit **low thermal conductivities than water**.
- *k* reductions depend on **dispersed components** but also on **droplet size** and **shape**.

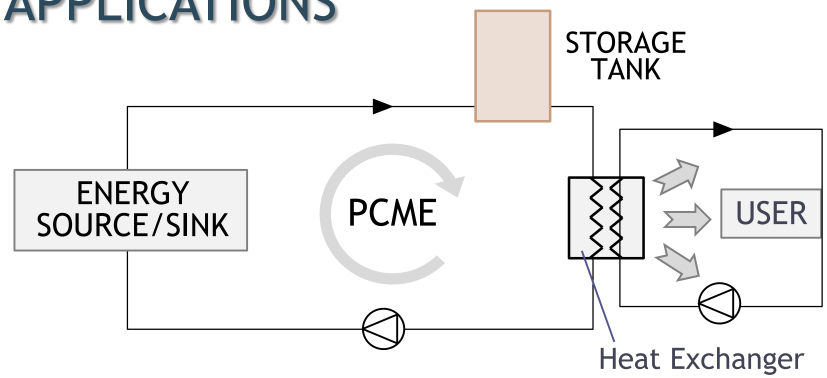


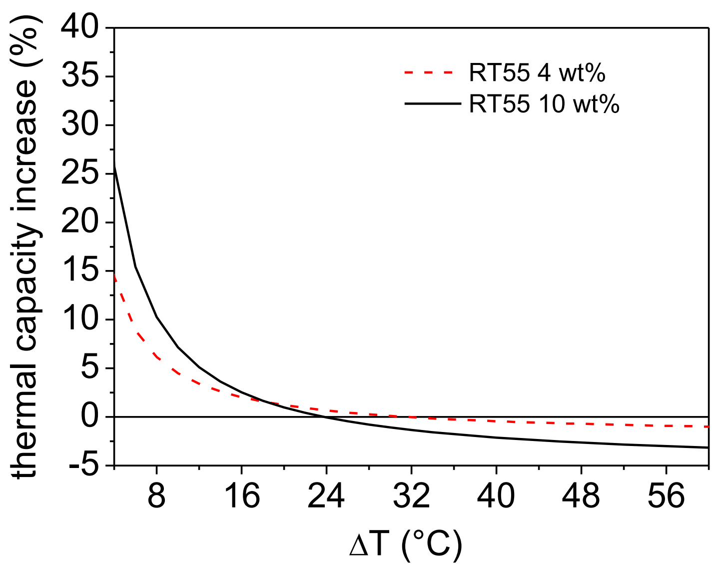
F Agresti, A Ferrario, S Boldrini, A Miozzo, F Montagner, S Barison, C Pagura, M Fabrizio Thermochimica acta 619, 48-52

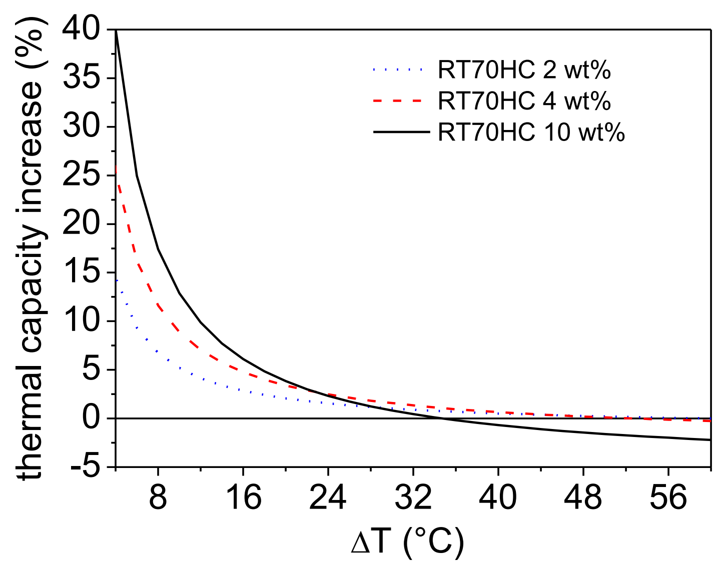




- PRACTICAL APPLICATIONS



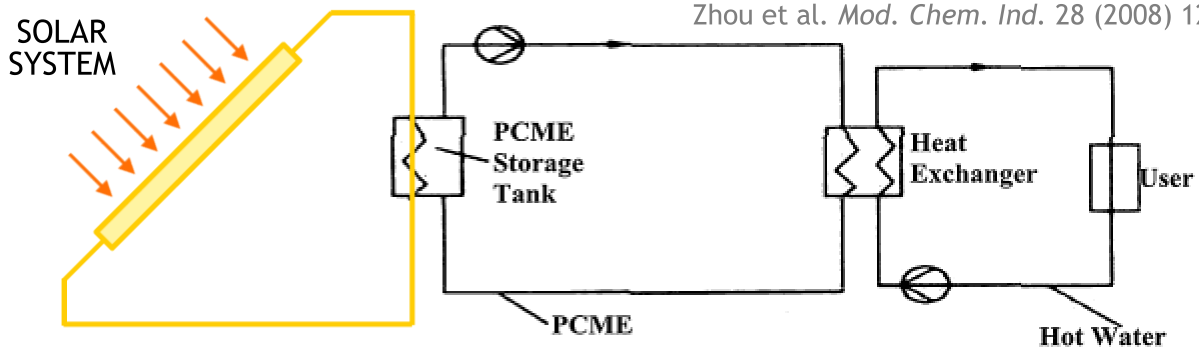




- With appropriate melting temperature, **PCMEs** are **potential secondary fluids for almost any thermal application** which requires:
  - ↑ Heat storage.
  - Heat supply at almost constant temperature conditions.
- **PCM** not only in the Storage Tank but **circulating**.

APPLICATIONS

HEAT STORAGE FOR HVAC OR DHW



Zhou et al. *Mod. Chem. Ind.* 28 (2008) 12-15.

- **Authors used a boiler** but it could be replaced by a solar collector.

	Hot water	Phase change emulsion
Equivalent specific heat (kg/kgK)	4.2	6.6
Volumetric flow rate (%)	100	67
Flow velocity (m/s)	3	2
Viscosity (mPas)	0.4	4.1
Friction loss per unit length (%)	100	83
Pump power consumption (%)	100	55

C28(30 wt.%)/W

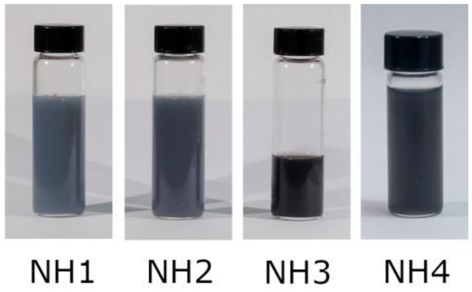
- PCME **specific heat 1.5 times** that of water → it is possible to deliver the same amount of heat with a **volume flow 33% lower** → **pump consumption reduces by 45%.**

APPLICATIONS

DIRECT ABSORPTION OF SOLAR RADIATION

- Absorptive properties can be enhanced by dispersing carbon nanostructures in:
  - Continuous phase
  - Dispersed phase.

Bortolato, Dugaria, Agresti, Barison, Fedele, Sani, Del Col.
Energy Conversion and management (2017) 150, 693-703



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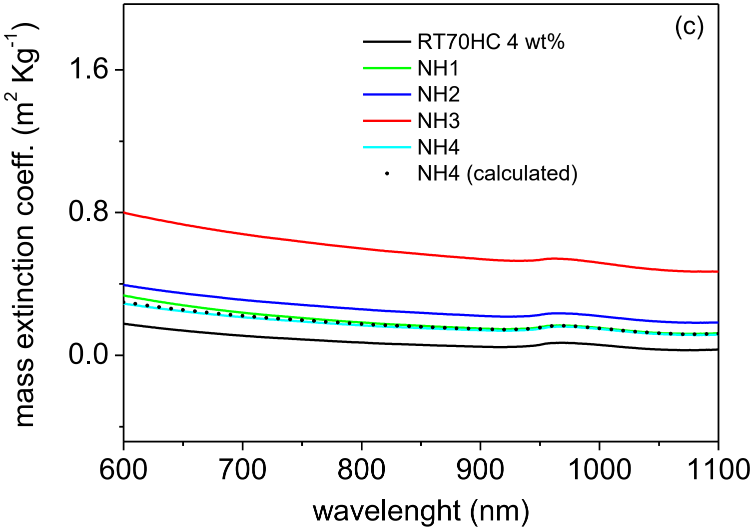

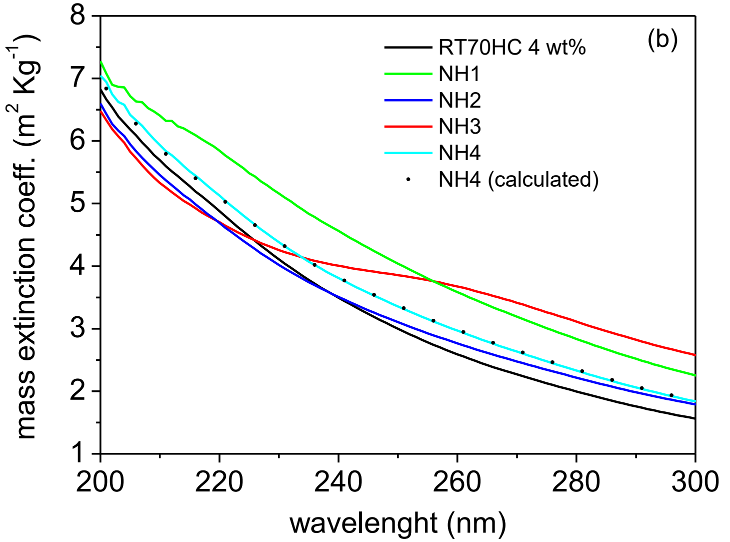

FUTURE REMARKS

- Practical **implementation of PCMEs in solar thermal applications** as cooling/heating media and thermal storage materials **seems feasible**.

- **However,** some **PROBLEMS must be faced** before a competitive edge over conventional carrier fluids.

  - **Stability** must be studied and improved to ensure reliable and long periods of usage.
  - **Sub-cooling** needs to be controlled and reduced to enhance system performance.
  - **Viscosity** increases must be moderated to minimize pumping power.
  - **Heat transfer performance** with phase change still needs a more comprehensive investigation.

- More **combined studies** on stability, sub-cooling and viscosity are required since these three properties are somewhat related and a balance among them is essential.