Looking for “low cost” Phase Change Materials and their application for energy saving.

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Abstract

Although technical viability of Thermal Energy Storage systems using Phase Change Materials (PCM) as storage medium has been proven, the economical viability holds its establishment back. Material cost is the critical point to enable their commercial expansion.

Since Thermal Energy Storage systems with PCM can contribute to the reduction of energy consumption in buildings or industrial applications, the establishment of such systems in the market is a goal for the scientific community.

Up to now, the search of adequate PCM was focused on the optimal behaviour of the material. Previous results indicate that a good thermal design of the heat exchanger makes up for the poor thermal properties of the PCM. The work was accomplished in the application to PCM direction: once an application was selected, the PCM was searched. Reversing this direction, this work focused on the methodology to complete a characterization of substances to evaluate their suitability of being used as PCM and looking for the application.

A list of waste materials of industry with potential use as PCM is performed. The most interesting materials are selected and first results of thermal properties are obtained

1. Introduction

Technical viability of Thermal energy storage systems using phase change materials as storage medium has been proven. The critical point to enable their commercial expansion is the material costs [1]. Up to now, the search of adequate PCM was focused on an optimal behaviour of the material [2, 3, 4]. Properties like narrow phase change temperature range or high energy storage density were fixed as the selection criteria. Non pure substances normally differ from these restrictions. Therefore, for a specific application only few materials satisfied the optimal properties [5] and normally the cost of these PCM are high.

Meanwhile the energy market do not include the environmental costs or environmental indicators are not use to fix the energy costs, the economical viability for most of the sustainable energy alternatives is not achieved compared to conventional systems.

Since Thermal Energy Storage systems with PCM can contribute to the reduction of energy consumption in buildings [6] or industrial applications, the establishment of such systems in the market is goal for the scientific community.

2. Material searching

Waste and natural materials are the main low cost products. The searching criteria were:

- Homogeneous material are needed to have a representative sample
- Phase change temperature range between -15ºC and 600ºC (temperature limits of most applications requirements)
- Non corrosive and non flammable (safety requirements)

Different sources were consulted using these criteria and some potential PCM were found.

2.1. IPPC permit database

An Integrated Pollution Prevention And Control (IPPC) permit is required for those companies listed in the annex of the current regulations based on the regulation 96/61/CE. This permit gather the authorized limits for each installation, energy, fuel and raw materials consumption, waste generation, emissions, noise and spillages. These IPPC permits are published. Therefore, the information about the waste material production for each company is available. In Aragon Region (Spain) the IPPC permits are published in the Official Region Bulletin (BOA) and the Aragon Government web [7] can be used to search this permits.

A first review of the IPPC permits was accomplished and some samples were obtained: used oil for cooking, hydraulic oil and cutting fluids.

2.2. Construction waste catalogue (CEDEX)

A Spanish Institute for Public Works (CEDEX) developed a catalogue of waste that can be used as construction materials [8]. All the products listed in the catalogue have melting points over 600ºC, so they are discarded for use as PCM. Nevertheless, a sample of a plaster waste from the process of phosphoric acid production was requested. This product is a hydrated salt ($CaSO_4$ $2H_2O$).

2.3. Request in forum

Waste materials with potential interest as PCM were request in different forums and to other research groups.

- Spanish Network for Thermal Energy Storage
- Aragón Institute of Engineering Research (I3A)
- Other research groups

Table 1 shows the search results

Waste	Source	State at room temperature
Used hydraulic oil	IPPC permit from an agri-food industry in Aragon (Spain)	Liquid
Used Oil for cooking		Liquid
Cutting fluid		Liquid

Waste	Source	State at room temperature
Plaster (From H_3PO_4 production process)	**Construction waste catalogue**	**Solid**
Glycerin 1 (from biodiesel production)	**Forums** **Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica Campinas, SP - Brasil**	**Liquid**
Glycerin 2 (from biodiesel production)	**Forums** **Thermochemical processes research group I3A**	**Liquid**
Glycerin 3 (from biodiesel production)		**Liquid**
Bio-oleo (from biomass pyrolysis	**Forums** **Bioware (Brasil)**	**Doughy**
Paraffin 1	**Forums** **Repsol (Spanish Network for Thermal Energy Storage)**	**Solid**
Paraffin 2		**Solid**
Paraffin 3		**Solid**
Paraffin 4		**Solid**

3. Thermal properties characterization:

3.1. Methodology

Following paragraphs describe the methodology for material characterization.

- Phase change temperature range determination

Liquid samples at room temperature are cooled down up to 5ºC during 24 h in order to corroborate that at 5ºC it is in solid state. In case it remains liquid, the same process up to -15ºC is accomplished. In case it remains liquid, the sample is discarded because it is out of the temperature range of interest for main applications.

- Sample behaviour

Solid samples at room temperature are heated up using an oven or a heat plate. The objective is to determine if the sample can be melted without any dangerous or harmful effect.

- Enthalpy vs. Temperature curves determination

Enthalpy vs. Temperature curves of the samples are the most important information about the potential use as PCM. First of all, these curves are obtained during heating. Afterwards, the curves are obtained during cooling for those materials with useful enthalpy values.

- Thermal cycling

Repeated melting and solidifying cycles are carried out in order to study if thermal properties remain or are modified.

- Enthalpy vs. Temperature curves determination after thermal cycling

The Enthalpy vs. Temperature curves determination after thermal cycling is used to discard those samples whose storage capacity decrease when repeated melting and solidifying processes took place.

- Thermal characterization

For those materials which thermal stability is proven, their thermal characterization is completed.

  - Thermal conductivity determination.

The specific heat of the samples is measured using a DSC 200 F3 Maia (NETZSCH) and Thermal Diffusivity is measured using a LFA 457 device (NETZSCH).

Thermal conductivity is obtained by applying equation 1.

$$\lambda = \rho \bullet cp \bullet \alpha \qquad \text{Eq.1}$$

where λ is the thermal conductivity [W/(m•K)], ρ is the density [kg/m^3], cp is the specific heat [kJ/(kg•K)] and α the thermal diffusivity [m^2/s].

  - Viscosity determination

Viscosity is critical parameter for pumpable PCM. Viscosity is measured at different shearing rates and at different temperatures using a ARG2 rheometer (TA Instruments).

3.2. Testing results

This works presents results up to thermal cycling.

Sample mode with sensibility and temperature calibration files is used to obtain the enthalpy vs. temperature curves. For peak detection were accomplished heating measurements.

For the Plaster (From H_3PO_4 production process) sample heating and cooling measurements were carried out to study the reversibility of intramolecular water losses.

Table 2 shows the measurements results.

Table 2: Measurement results

Sample	Temperature range	Results
Used hydraulic oil	**-**	**Still liquid at -15ºC. Discarded.**
Used Oil for cooking	**-30ºC to 30ºC**	**Low peak between -10ºC and 0ºC. 89 J/g is the enthalpy obtained by peak integration. Discarded due to low energy storage capacity compared to water.**
Cutting fluid	**-30ºC to 30ºC**	**Peak observation at 0ºC, might be due to the water contain.350 J/g is the enthalpy obtained by peak integration. Discarded due to low energy storage**

Sample	Temperature range	Results
		capacity compared to water.
Plaster (From H_3PO_4 production process)	**90ºC -235ºC-80ºC-235ºC**	**Non-reverse water losses during first heating. 500 J/g is the enthalpy obtained by peak integration. Discarded due to no reversibility.**
Glycerin 1 (from biodiesel production)	**-25ºC to 20ºC**	**Low energy peak between -9ºC and -2.2ºC. 8 J/g is the enthalpy obtained by peak integration. Discarded due to low energy storage capacity.**
Glycerin 2 (from biodiesel production)	**-30ºC to 0ºC**	**It is the same sample than glycerine 3, but the methanol was removed. Liquid at -15ºC. Discarded.**
Glycerin 3 (from biodiesel production)	**-30ºC to 0ºC**	**Methanol and sodium methoxide impurities low down the melting point. No peaks are detected. Discarded.**
Bio-oleo (from biomass pyrolysis)	**-**	**Liquid at -15ºC. Harmful gases are emitted when heated. Discarded.**
Paraffin 1	**-10ºC to 100ºC**	**Result details shown in following section.**
Paraffin 2	**-10ºC to 100ºC**	**Result details shown in following section.**
Paraffin 3	**-10ºC to 100ºC**	**Result details shown in following section.**
Paraffin 4	**-10ºC to 100ºC**	**Result details shown in following section.**

4. Results analysis: Potential applications

Paraffins provided by Repsol are the only samples with interesting results. Table 3 show the melting temperature ranges.

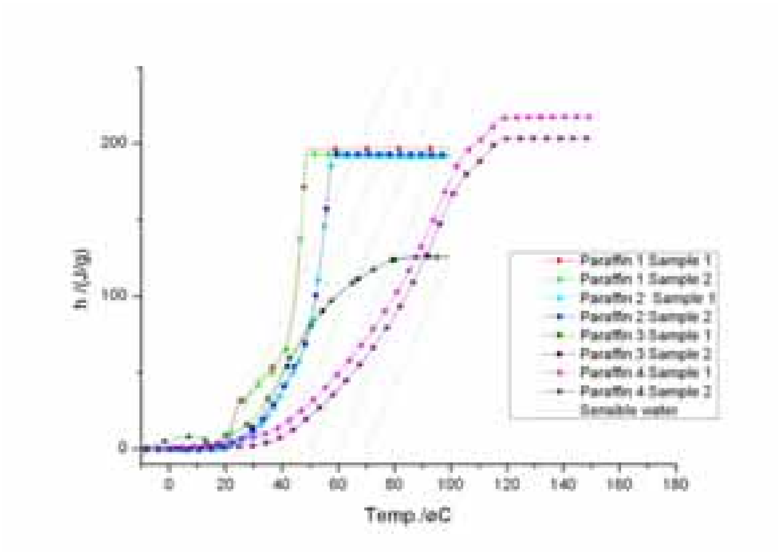
Table 3: Melting temperature ranges and testing conditions

Sample	Melting temperature range* (ºC)	Mass (mg)	Temperature program (ºC)	Heating rate (K/min)
Paraffin 1	**40 -48**	**24.83 / 19.2**	**-10ºC to 100ºC**	**0.5**
Paraffin 2	**57.6**	**20.41 / 26.49**	**-10ºC to 100ºC**	**0.5**
Paraffin 3	**77.1**	**21.67 / 27.56**	**-10ºC to 100ºC**	**0.5**
Paraffin 4	**114**	**34.69 / 31.14**	**-10ºC to 100ºC**	**0.5**

* Given data by the manufacturer

Figure 1 shows enthalpy vs. temperature curves of the paraffins compared to water.

Figure 1: h vs T curves (heating) compared to water (sensible heat).



Parraffins 1 and 2 are the most interesting ones. Therefore, heating and cooling curves were obtained. Figures 2 and 3show the results:

Figure 2: h vs T curves the parafins 1 y 2 (heating)

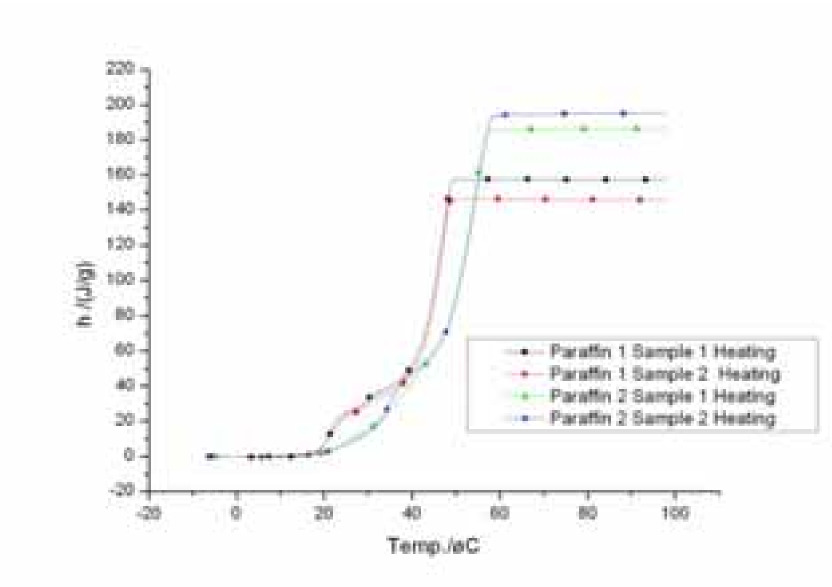
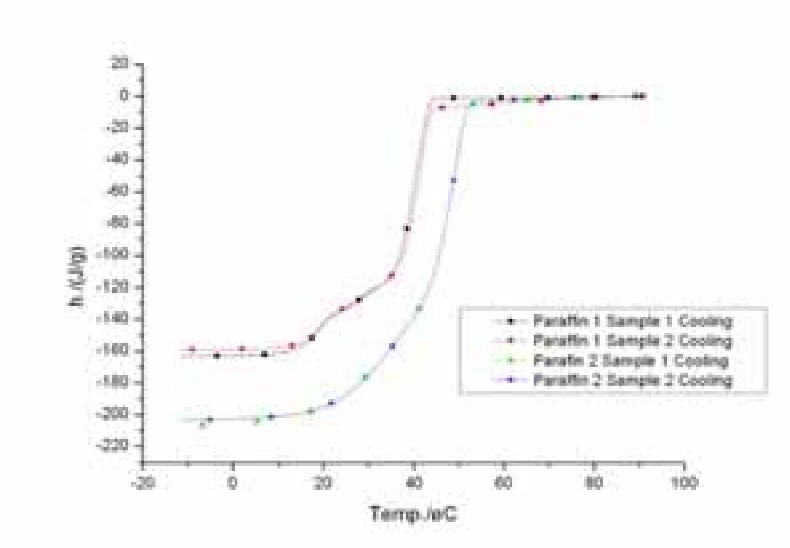


Figure 3: h vs T curves the parafins 1 y 2 (cooling)



Zalba et al.[3] shows the potential applications for PCM as thermal storage materials.

Table 6 shows potential application for each of the selected paraffins due to their temperature range [3].

Table 6: Examples of potential applications for paraffins 1 and 2

Sample	potential applications
Paraffin 1	**- Thermal protection of electronic devices (integrated in the appliance)** **- Domestic hot water tanks** **- Fire safety dresses (fire retardant addition needed)** **- Fire protection of building structures (fire retardant addition needed)** **- Cooked food transportation (pizzas, catering,..)** **- Inertia tanks for low temperature heating systems** **- Inertia tanks for water from a recovery boiler in a cogeneration plant**
Paraffin 2	**- Thermal protection of electronic devices** **- Domestic hot water tanks** **- Inertia tanks for low temperature heating systems** **- Inertia tanks for water from a recovery boiler in a cogeneration plant**

Next, the described methodology will be completely applied for paraffin 1 and 2 characterization.

5. Conclusions:

A methodology is proposed to find and characterize waste material as potential phase change materials for thermal energy storage. This methodology was partially applied and first results are shown in this work. Next, the methodology will be completely applied for paraffin 1 and 2 and more samples will be search in different sources.

The objectives of this methodology are:

- Finding low cost materials to enable the commercial development of PCM applications
- Gaining value of waste or by-products avoiding its placement in a dumping site and achieving an environmental profit.

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- A H_3PO_4 production company provided the plaster samples.
- Bioware provided bio-oil.
- Research groups from Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica Campinas, SP – Brasil and Thermochemical Processes research group (I3A, Spain) provided glycerin samples.

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