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EXPERIMENTAL INVESTIGATION OF THERMAL STORAGE USING WASTE MATERIAL



Relatore

prof. Papurello Davide

Candidato

Tommaso Pavone

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ABSTRACT

The study, which will be described in the following chapters, focuses on the energy feasibility of organic waste materials for their possible application in thermal storage systems as phase change material.

First, we have briefly described the generality of possible energy storage solutions, focusing mainly on the thermal storage systems. Thermal energy storage (TES), with various types of phase change materials, were investigated considering the exploitation of their latent heat. Among the commercial materials, it was chosen a paraffin wax, while as innovative materials were chosen fatty materials of animal origin. This is a circular material approach in order to reuse also such kind of wastes from kitchens and restaurants refuses. The products chosen for the analysis are lard, butter and animal fat obtained from a previous cooking phase. This last material has been chosen in such a way that, unlike the others, it is possible to determine if an organic waste can be an optimal solution for the thermal storage in order to lower the investment costs for the storage thermal system.

Furthermore, it was decided to carry out the same procedures with paraffin, which, in the phasechange thermal accumulations, is the most used material for these types of systems.

A first phase of laboratory tests was carried out. This makes possible to check whether the chosen materials are able to reach the temperatures typical of a TES system and if at those values, the materials chosen reach the melting temperature for the latent heat storage.

A second test phase consists in the scaling simulation of a TES system. It consists in the introduction of a further layer of the phase change material to simulate a possible accumulation phase.

Experiments were carried out in laboratory, with a specific test rig and, in parallel such experiments were simulated using COMSOL Multiphysics 4.3a software.

These simulations have been made in such a way as to be able to reproduce a more ideal situation of the built systems and to check how far they differ from the analyzes carried out in the laboratory.

Furthermore, with the help of the Applied Science and Technology Department (DISAT), materials were analysed using the DSC (Differential Scanning Calorimetry) study. This analysis was used to calculate the latent heat storage, the temperature of melting and solidification. Subsequently, these data were used for the evaluation of the specific heat at constant pressure that the material assumes during the charging and discharging phase.

This has served to verify and to quantify such materials at the operating temperature of a typical domestic hot water request (DHW). This energy would be useful to understand if the materials considered can be excellent substitutes in the thermal storage systems to the phase change materials generally used.

SUMMARY

1. INTRODUCTION	. 1
1.1 STORAGE SYSTEMS	. 2
1.2 TYPES OF STORAGE SYSTEMS	3
1.3 THERMAL STORAGE	. 7
1.3.1 SENSIBLE THERMAL STORAGE	. 8
1.3.2 LATENT THERMAL STORAGE	10
2. LATENT HEAT STORAGES	12
2.1 TYPOLOGY OF MATERIAL	12
2.1.1 INORGANIC MATERIALS	13
2.1.2 ORGANIC MATERIALS	15
2.1.3 EUTECTIC MATERIALS	17
2.1.4 NON-EUTECTIC MATERIALS	18
2.2 TYPES OF APPLICATION	19
3. ORGANIC PHASE CHANGE MATERIAL	22
3.1 ORGANIC PARAFFINIC MATERIALS	23
3.2 NON-PARAFFINIC ORGANIC MATERIALS	26
3.3 NON-PARAFFINIC ORGANIC MATERIALS EXAMINATED	29
3.3.1 LARD	29
3.3.2 BUTTER	30
3.3.3 MEAT FAT	35
3.3.4 PARAFFIN WAX	36
3.4 DSC ANALYSIS	37
4. EXPERIMENTAL PHASE	43
4.1 TESTS ON SMALL SYSTEM	44
4.1.1 MATERIAL UESD	44
4.1.2 ASSEMBLY PHASE	45
4.1.3 SIMULATION WITH COMSOL MULTIPHYSICS SOFTWARE	51
4.2 EXPERIMENTATION IN SCALE	59
4.2.1 MATERIAL USED	59

4.2.2 ASSEMBLY PHASE	60
4.2.3 SIMULATION THROUGH COMSOL MULTIPHYSICS SOFTWARE	66
5. RESULTS	71
5.1 SMALL THERMAL STORAGE	72
5.1.1 LARD	72
5.1.2 BUTTER	79
5.1.3 PARAFFIN WAX	85
5.1.4 FAT	92
5.2 SCALE REPRODUCTION	99
5.2.1 LARD	99
5.2.2 BUTTER	105
5.2.3 PARAFFIN EAX	110
5.2.4 FAT	116
5.2.5 AIR	121
5.3 RESULTS OF THE DSC ANALYSIS	125
5.3.1 LARD	126
5.3.2 BUTTER	128
5.3.3 PARAFFIN WAX	129
5.3.4 ANIMAL FAT	131
6. CONCLUSIONS	133
BIBLIOGRAPHY	138

1. INTRODUCTION

The uncontrolled use of fossil fuels in industrial production processes has led to a substantial increase in greenhouse gases (GHG) of CO₂ and CO into the atmosphere.[1]

These emitted gases create extensive natural damage, primarily global warming, as greenhouse gases, triatomic and diatomic molecules create the phenomenon of absorption and scattering of solar rays.

The first one would correspond to the absorption of solar rays by the triatomic molecules and the greenhouse gases. This will avoid that the sun's rays, reflected from the earth's surface, are released into space. The scattering phenomenon would correspond to the reflection, by the diatomic molecules, of the reflected solar rays coming from the Earth's surface.

These phenomena, therefore, have caused, especially in recent years, an increase of temperatures that have caused damage to the Arctic ice cap with a reduction in its extension. This will cause the rise of sea levels and the deep damages of crops due to the uncontrolled weather changes.

Through previous studies, it has been established that, since 1751, the various industrial chains have issued approximately 347 billion tons of gas. That is why, especially in recent years, we are trying to study and to apply alternative energy processes that are especially low emissions of harmful gases. It is mainly talking about renewable energy sources from which they are obtained from natural sources present in nature: solar, geothermal, hydroelectric and wind energy.[1]

Among the sources mentioned above, the most interesting is the solar source. The International Energy Agency (IEA) estimated that in 2050, 21% of the world's electricity produced will come from solar sources.[1]

In the last 3 years, the production of energy produced from solar sources has increased by 35% and, despite still having a very low share compared to the remaining renewable sources. [2]

While in 2050, 16% of the thermal energy used for heating and cooling of buildings will be covered by solar thermal systems.[3]

However, the use of solar systems, both thermal and photovoltaic, finds problems of various kinds: the intensity of solar radiation varies with the geological position, daily and the seasonal period, but above all depends on local weather conditions. In fact, a negative factor in the energy systems that use the solar source is the fluctuating variation in the hours of light and darkness.

This problem is relevant, above all for this technology, precisely because the highest peaks in the demand for thermal and electrical energy are mainly in the dark hours where it is not possible to make full use of renewable sources with solar energy.

This fluctuation of thermal and electrical energy demands is found in high energy production applications from renewable sources.

The accumulation function has been introduced to deal with this disadvantage and reduce the gap between production and demand of energy.

In fact, the primary purpose of placing the storage system in the energy production system is to increase efficiency.

The accumulation system has been more incentivized, in the last few years since we have obtained excellent results, also from the economic point of view.

1.1 STORAGE SYSTEMS

As already mentioned above, one of the main disadvantages of renewable energy source systems is the variability and the difficulty of matching between the energy demand and its production. In fact, the phases of greater energy demand, mainly thermal and electrical, occur in periods when there are low quantities of energy producibility; just as there are daily periods in which the opposite effect occurs.

A huge waste of energy occurs. This is caused by the amount of unused energy that is dispersed in the environment.

It is for this reason that storage systems are believed to play a key role in the renewable energy production plant, to obtain greater availability and economic advantage of intermittent sources in order to meet the energy demand.

Benefits that will be obtained adopting an accumulation system for a RES plant are:

- Reduction of energy costs;
- Reduction of energy consumption;
- Greater operating flexibility;
- Reduction of initial investment and maintenance costs;
- Reduction of dimensions of production plants;
- Increased energy efficiency;
- Reduction of the environmental impact of energy generation systems.[4]

1.2 TYPES OF STORAGE SYSTEMS

A generic energy process is mainly subjected to losses and through certain energy storage techniques is possible to compensate for the low flexibility of fuels for the benefit of others. The thermal storage is one of the most used energy storage system. A portion of thermal energy that can be lost is reused for a secondary purpose.

For each type of application we tried to apply the most appropriate storage system solution:

a) Mechanical and hydraulic systems

One of the first mechanical energy storage application system is the flywheel whose main purpose is to limit the excesses of mechanical energy on total mechanical work in periodic machines.

The flywheel is mainly opposed to any variation in its angular velocity, trying to obtain a stability of the rotation of the driving shaft when a periodic driving torque is applied.



Figure 1Typical flywheel [4]

Moreover, it is exploited for the accumulation of mechanical energy produced by an engine that delivers low power for a long period, and then releases it to higher powers in shorter periods. With regard to this the flywheel has as its fundamental principle, that of accumulating the mechanical energy produced by the rotation of the tree in kinetic energy. This particular conversion was then exploited in other application fields, such as reversible electric machines in the field of propulsion and transport.

While for the hydraulics sector, one of the most intuitive systems for accumulation is the pumping system.

The pumping system consists in pumping water from the valley upstream at night when the energy demand is lower and the electricity costs are lower, and sent downstream during the day when there are greater peaks of electricity.[4]



Figure 2 Pumping process during the day



Figure 3 Pumping process during the night [5]

b) Compressed air storage

This type of application is used in periods of low electricity demand and therefore exploiting the excess energy produced by the plant. In the post-compression phase, the air is stored in an underground cavity and then withdrawn in periods of greater energy demand.

So during the night, when the cost of electricity is low, we try to compress as much air as possible to generate electricity, taken from the grid, during the compression phase.

During the night the cost of electricity is higher, and then the compressor must work for short period. In this case, the compressor is the component that needs the greatest amount of energy taken from the electricity grid.

So compressed air is stored in the underground quarry at an almost constant pressure of around 70 bar.

During periods of peak demand, the air is released and heated with natural gas or with compressed air coming from the compressor, and then it is expanded inside the turbines.[6]



Figure 4 Typical CAES system [7]

c) Electrochemical batteries

This type of accumulation system is the most common and readily available solution. It accumulates energy in the form of chemical energy and releases it as electricity.

Batteries are equipped with high stability energy and power density. The most common type of battery is the Pb/acid.

They are used in many types of applications, including heat load management, electric vehicles and renewable energy storage.

They can easily replace the pumping or compressed air systems when the demand capacity is limited.

This accumulation system has a good efficiency that is between 70-80%.

d) Magnetic storage

Energy can also be stored in the form of magnetic energy, created by the passage of current inside a coil, consisting of a semi-conductive material, subjected to cryogenic techniques.

To increase the amount of energy that can be stored and the speed of energy storage, the same procedure can be carried out using high-performing superconducting materials.

These materials are characterized by an electrical resistance considered negligible which determines a leak-free current flow. However, these losses will be considered when a current from alternating current is carried out and a loss of 10-20% occurs.

e) Hydrogen production as storage tool

Hydrogen is not first considered as a source but as an energetic vector, since there is no need for a preliminary phase of production of the gaseous material since there is no pure in nature. Hydrogen is considered as a very interesting energy carrier because it is possible to store it and transport it very easily.

The negative factor to consider for this material is the fact that the costs of electricity, on which we must go to save during periods of peak demand, are lower than the cost of the electricity itself exploited for the production of hydrogen itself.

One of the major difficulties in the use of this gaseous material as an energy carrier is the accumulation phase itself, since to accumulate it requires a large amount of storage space and high-performance materials that can contain the hydrogen within the control volume.

It is for this reason that to make the storage phase less problematic it is possible to liquefy the gaseous material to make the fluid more inert and the possibility of leakage and breakage of the containment material being less risky.

f) Thermal storage

The thermal storage phase is one of the most used and easiest to reproduce systems among the various storage systems mentioned above. This storage technology determines the possibility of storing large quantities of thermal energy and then reusing them in successive phases. The thermal energy can be accumulated in various forms but in this case we tried to carry out a more detailed study in the following chapters.

1.3 THERMAL STORAGE

Thermal storage systems can be grouped into two types depending on the type of material used as energy vector for the thermal storage phase.

The accumulation system that causes the variation to increase the temperature of the material is called sensible storage; while the accumulation of heat that causes the phase change of the material is called latent storage.

Principally, the storage system is designed to operate cyclically by applying a classification on the type of storage duration.

- Short term accumulation: exploited mainly to cope with peaks in heat energy requests of a few hours per day. This system is mainly used to reduce the size of the energy production plants but above all to take advantage of the cheaper hourly rates.
- Medium or long term accumulation: mainly used to conserve heat over longer periods of time ranging from a few weeks to months.

The long-term ones, above all, take advantage of seasonal climate changes. These types of accumulation for medium and long-term purposes have efficiencies that are around 70% compared to 90% of short-term systems.[4]

Another possible classification mode is based on the operating temperature. The reference temperature of these storage systems is $120 \degree C$. In fact, if the operating and storage temperature has a temperature lower than $120 \degree C$ these accumulations are part of the low temperature accumulations. These systems mentioned above are interesting because the losses are more contained and therefore require lower thermal powers.

As mentioned previously, thermal storage systems are widely used and are basically designed to operate cyclically and would therefore entail beneficial purposes when they achieve the following purposes.

- Increase generation capacity, which would consist in the application of an energy production unit that its main objective is not to cover the peaks of energy demand but to work at higher power loads;
- Increase in the operation of cogeneration plants, which would therefore allow the cogeneration system to free itself from the demands of the load curve;
- Purchase of electricity at the most economically convenient times;
- Improved reliability of production systems;
- Integration with other energy alternatives.[4]

1.3.1 SENSIBLE THERMAL STORAGE

For the first type of storage system, the amount of thermal energy is commonly stored in the water.

It is used for its modest costs, for its easy availability, for its high specific heat, for the easy transport and for the short transmission duration of heat.

The design phase of the storage tanks is fundamental. In fact the purpose is to create tanks that are able to maintain optimal thermal stratification and thermal insulation from the outside.

The generic thermal storage process can be composed of three steps:

- Charge phase;
- Storage phase;
- Discharge phase.



Figure 5 The three phases of a typical storage[4]

Thus, in summary, the main purposes of the storage tanks for sensible storage are:

- Guarantee of thermal stratification, which consists in a clear diversification and separation between zones at different temperatures. In fact, it is essential to try to avoid mixing the zones at different temperatures as it would cause an increase in the probability of thermal dispersions towards the outside;



Figure 6 Stratification into sensible thermal storage[4]

- Minimization of dead zones;

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Figure 7 Dead zones in thermal storages[4]

Minimization of losses and infiltrations of heat towards outside.[4]

1.3.2 LATENT THERMAL STORAGE

Latent thermal storage systems represent the most interesting alternative to the sensitive heat storage system. In general, it consists of a material that exploits the amount of heat used to chance its phase of material (PCM).



Figure 8 Difference between sensible (a) and latent(b) heat storages [8]

Therefore the material, used for this type of application, is a phase change material in which the temperature remains constant during the storage period, and therefore at the second step of the cycle.

From the figure 8, it is possible to notice how the latent heat storage system mainly exploits the central phase, in which the phase change material develops and where the temperature remains constant.

The latest studies consider and treat the advantageous properties of PCMs that would allow a wide possibility of application in order to have a better alternative to other types of storage systems.

Unlike any material used for a sensible heat storage system, the phase change is characterized by a high latent heat and specific heat that would allow it to accumulate as much heat energy as possible.[9]

One of the major disadvantages of PCM is their low conductivity which makes the process slower and therefore one of the main purposes is to increase the speed of heat transmission in the medium to make the charge and discharge phases faster.[10] So in the subsequent studies we will make a study more in depth those characteristics that will be increased in order to improve the various phases.

Unlike a sensible heat storage system, where one of the main purposes is to maintain a thermal stratification along the entire control volume, the latent heat can be decomposed into several zones at different melting temperatures, so as to satisfy more loads at different temperatures.



Figure 9 Difference between stratification of sensible heat storage and temperature zones od PCMs [10]

For a good sizing of a latent heat storage system with phase change material it is recommended to take into consideration the following characteristics:

- Range of temperature of the storage system and the fluid flow rate for the thermal exchange;
- The type and characteristics of PCM;
- Matching between the amount of energy accumulated and released by the system;
- Comfort requirement.

In summary, it is possible to determine the elements that characterize the choice of a PCM:

- a) Thermo-physical properties:
- Easiness of choice of material based on the operating temperature range;
- High conductivity good heat transmission properties;
- High latent melting heat per unit of mass;
- Thermal stability;
- Phase stability and no segregation;

- Low volume for the charging phase;
- Low saturation pressure at operating temperature;
- b) Kinetic properties:
- High degree of nucleation and no undercooling in the liquid phase;
- High degree of crystallization;
- c) Chemical properties:
- Complete fusion and solidification cycling;
- Long-term stability and lack of degradation after several melting and solidification cycles;
- Chemical stability;
- No toxicity, flammability and explosiveness;
- d) Economic properties:
- Abundance and availability;
- Low economic value;
- e) Environmental properties:
- Low energy incorporated;
- Easy separation from other materials and recycling potential;
- Low environmental impact and low pollution.[11]

2. LATENT HEAT STORAGES

As already well defined above, the storage system is mainly used by renewable energy plants. Phase change materials must have specific properties including the melting and solidification temperature that must be in accordance with the type of application on which to install the storage system.

2.1 TYPOLOGY OF MATERIAL

Considering several literature studies carried out, it was determined a precise classification of phase change materials used.

The PCMs of interest are divided into:

- Inorganic;
- Organic;
- Eutectic;
- Not Eutectics.



2.1.1 INORGANIC MATERIALS

As shown in the above graph, the main inorganic PCMs are subdivided into hydrated salts and metals.

Regarding the first category, hydrated salts are one of the most used as phase-change accumulation material among inorganic ones.



Figure 10 Hydrated salts (a), metals (b)[12]

Regarding this material, this can be considered as a material that works at medium-low temperatures, and therefore they are highly exploited precisely because they can be applied to a large quantity of energy applications.

Like any phase change accumulation material, in contact with a hot fluid it takes heat and then releases it with a cold fluid and with this last process the material is characterized by the crystallization of the body.

One of the most important disadvantages of hydrated salts is the under-cooling which is mainly due to the speed at which the heat release phase occurs.

Another inorganic material belonging to this category are the molten salts which are characterized by a low thermal conductivity and that is why the accumulation component is optimized by mixing them with materials, of metallic nature, or the duct, in which the fluid passes, is integrated with a finning to increase the heat exchange surface.

The other category belonging to phase change accumulation materials are metals that, unlike previous materials, have a high thermal conductivity and a high latent heat.

Having these particular properties the material works at much higher operating temperatures and having excellent thermal conductivity, the probability of dispersion of heat towards the outside of the control volume is much higher, and therefore to avoid this inconvenience the volume containment material is integrated with a thick layer of insulation to contain losses.[9] Based on the studies carried out, it was possible, especially for hydrated salts, to identify the advantages of using the material in a storage system:

- High heat of volumetric accumulation and high melting enthalpy;
- High melting heat;
- Quick exchange phase;
- High thermal conductivity;
- Flammability;
- Possibility of using small exchange volumes;
- Compatibility with plastic materials;
- The use of hydrated salts is preferred to organic materials as paraffin to obtain a better reduction of environmental impact in the manufacturing phase;

In addition, always through the studies carried out on the hydrated salts, as well as the other inorganic accumulation materials, we have highlighted the disadvantages that would make the accumulation process less efficient:

- Low nucleation properties and under-cooling problems;

- Inconsistencies in the temperature of function during the various charging and discharging processes;
- During the transition phase, problems of segregation and thermal instability occur;
- Increase, during their repeated exploitation, of degradation;
- Incompatibility with some materials used for building construction, because if we install the inorganic PCM with some building components, it would make the opaque envelope of the building more unstable;
- Corrosive with some metallic and slightly toxic materials.

2.1.2 ORGANIC MATERIALS

The organic materials, as regards the thermal storage system, becomes one of the most interesting components to be exploited.

As shown in the graph above, organic materials, to be used for thermal storage systems, are subdivided into two categories, paraffinic and non-paraffinic.

The first category are mainly hydrocarbons and are characterized by a good storage capacity. As for the category of not paraffinic storage materials, they are mainly fatty acids or, as we will see later, organic waste characterized by a good latent heat of fusion, an adequate operating temperature that can be used by many types of systems of energy production, especially from renewable sources.



Figure 11 Natural paraffin (on the left)[13], encapsulated paraffin (on the right)[14]

Through the studies carried out, to see its feasibility in the energy field, it was possible, as determined for inorganic materials, to identify positive factors in organic materials:

- Wide availability in a wide temperature range;
- High latent melting heat;
- Heat transfer and cooling of the material even for a small amount of energy and no possibility of under-cooling effects in the discharge phase;
- Phases of congruent phase changes;
- Good self-nucleating properties;
- No possibility of nucleation in phase change and good degree of nucleation.

Just as there are advantages, some disadvantages characterize the organic materials that must be tackled in such a way as to reduce negative effects and improve performance:

- Low thermal conductivity of fusion;
- Low latent volumetric heat capacity and low enthalpy quantity in the phase change period;
- Low volumetric density;

Some materials are flammable because some organic materials, especially paraffinic, are mainly hydrocarbons;

- High cost especially for paraffinic materials as their availability is low;
- High volumes, compared to inorganic materials, so that the heat exchange and accumulation phase is successful.

The organic materials used in thermal storage systems will be seen in more detail in the following chapter, as our study is based on the feasibility of using organic waste materials for thermal storage systems.[11]



Figure 12 PMCs with their Melting temperature and Heat of fusion[13]

As shown by the graph in the figure 12, while working at the same temperatures, the organic and inorganic materials have very different fusion enthalpies and as a function of this sharp difference, it is possible to apply different materials to the same energy systems.

Also from the previous graph, it is possible to notice one of the main differences between the organic and inorganic accumulation materials, that is, how the organic materials have a latent heat of fusion much lower than the inorganic ones.

2.1.3 EUTECTIC MATERIALS

The eutectic materials consist mainly of the mixture of two or more components where they are characterized by the same melting point.

These materials are practically used because a single material could have deficits that would make the accumulation phase poorly performing, and therefore mixing them with other materials with excellent energetic characteristics would make the whole component better and the whole process of energy storage more efficient.



Figure 13 Typical eutectic mixture[15]

As can be seen from the graph, it is convenient to make the mixture work near the eutectic point, where the same melting temperature is obtained and where it is possible to take advantage of the energetic characteristics of both the materials that make up the mixture.

Unfortunately, this component, compared to the previous two, is still under study because it is a difficult task to find a good compromise between two materials that have excellent energy performance. However, due to the simple fact that in order for the two mixed materials to operate at the same time they have limited use, that is, some energy systems that work at different temperatures from the melting point of the eutectic material cannot take advantage of the material itself.[11]

2.1.4 NON-EUTECTIC MATERIAL

As for this last category, it is mainly exploited in cooling energy thermal systems. In fact, the non-eutectic thermal accumulation materials are characterized by the mixture of different materials such as to give the whole heterogeneous component with different melting temperatures.

Based on the energy point of operation of the system that exploits the material, a well-defined melting temperature, which would consist of a melting temperature of one component of the mixture or another, will be taken into account.

Having different problems regarding the exploitation of the whole material, we try to use it at low temperatures in order to take advantage of the greatest number of beneficial factors of the mixture. And this is why non-eutectic material is mainly used in cooling systems.

The use of the component only for this type of energy systems, would make its goal much more limited and therefore could not be exploited by other energy systems at higher temperatures.

Moreover, its heterogeneity would make it more difficult to exploit both components of the mixture to the maximum and that is why the non-eutectic material is used at lower temperatures.[16]

Therefore, in conclusion, the component on which we are going to focus are non-paraffinic organic materials in such a way as to be able to verify if waste materials with energetic characteristics consistent with those of generic organic materials can have their use in the field of energy storage.

2.2 TYPES OF APPLICATION

Through the studies carried out, phase change materials can be used for a wide range of applications that mainly determine the possibility of being able to reduce energy production costs in economically unfavourable daily periods.

Phase change material is most often used to replace the simple materials used for energy storage for solar thermal systems.

These types of systems work mainly during the day trying to accumulate thermal energy in these hours, where the energy demand is lower, and then release it at night where the demand peaks are greater.

A limiting factor of the solar thermal plant is its intermittency and cyclicity which is disadvantageous for the thermal energy production phase. And this is why we tried to couple an accumulation system to the energy production system. An application that has been tried to develop in recent years is the possibility of being able to replace the typical storage systems with sensitive materials and with PCM, in order to reduce the costs of materials but above all space.[4]



Figure 14 Typical latent heat thermal storage coupled with solar thermal system

There are many factors to be considered for this application in such a way that the functioning of the thermal storage system, with phase change material, is effective is the melting temperature of the PCM. In fact, the melting temperature must be at least 5 °C lower than the temperatures reached by the solar thermal system, so that the entire material is melted and the greatest possible amount of thermal energy is captured. [17]

It has been ascertained that, with the introduction of a thermal accumulator based on phase change material, as well as with sensitive materials, the efficiency of the solar thermal system, the solar fraction would be increased and the cost of the whole system of production (solar collectors), but above all it would be possible to use the entire energy stored in dark periods where the demand for thermal energy is higher. However, through the use of the phase change materials, would also face a possibility of being able to reduce the spaces and, through the easy availability of the material, would reduce the costs of the accumulation material.

Another application on it is possible to apply PCM is the introduction of these phase change materials in the stratification of the opaque envelope of a building.

This installation aims to shift the thermal load peaks to which the building is subjected.



Figure 15 Thermal loads in a simple apartment [18]

In fact, both from the inside, with anthropic activities and electronic equipment, and from the outside, with weather stress, the entire opaque shell must have the possibility of being able to accumulate heat and then release it in daily periods when temperatures are more low, thus maintaining the highest internal temperature, thus reducing the use of the air handling unit and thereby reducing electricity costs.[18]

The main purpose is to increase the thermal accumulation inside the opaque casing and to do this, various options have been made regarding the positioning of the phase change material within the stratification of the wall.



Figure 16 Different application of PCM into the stratification [18]

Depending on the positioning, shown in the figure 16 above from layer 3, it is possible to favour the interior or exterior of the building. If the PCM is exposed to the inside and the insulating material more towards the outside would favour the inside of the building, thus releasing the heat, produced above all by the anthropic activities, at night.

Behzadi and Farid [19] carried out a comparative study between a building with PCM and one without and it was concluded that the daily fluctuation is reduced by 4 °C on summer days and highlighting a significant energy saving for the air conditioning system of 34.5% and 21% in the heating of winter days.

Finally, this possibility of introducing the phase change material inside the opaque casing has opened up numerous applications such as the PCM encapsulation inside the wall itself, or how to apply the PCM on the floor using the inlets or even in the pavement.



Figure 17 Macro PCM on the wall [20] and on the roof [18]

A last application that aroused much interest is to be able to replace the air treatment unit consisting of heat exchangers, in which cold or hot water passes depending on the season, time of day and internal loads, with the PCM thus applying a free cooling system. [21]



Figure 18 Free cooling process [18]

During the night the cold air is stored by the PCM through natural ventilation and then released into the living areas during the hours of light and heat, thus obtaining results with regard to energy saving. [22]

Through other studies carried out, it has been noticed that the thickness of the PCM inside the ventilation system plays an important role for the heat exchange, as well as the mass flow rate of the air passing through the PCM banks.

Finally, through the application study of various types of phase change materials within the ventilation system, it was stated that the energy saving of electricity compared to the traditional ventilation systems is about 73%. [23]

3. ORGANIC PHASE CHANGE MATERIAL

As already mentioned in the previous paragraphs, there are four macro categories of phase change accumulation materials. Among these, those that still present a scientific interest are organic materials.

Phase change organic materials are mainly divided into two: paraffinic and non-paraffinic.

Both categories of organic materials have lower thermal properties than other accumulation components. Just think, for example, that the latent heat of fusion of inorganic materials is higher than the organic ones if they are operated at the same operating temperatures.

However, their high availability in nature and their low cost make organic phase change materials a subject of study.

From the first comparative studies, it has been verified that most of the phase change organic materials are excellent to be exploited by energy systems that work at different operating temperatures.

Unlike inorganic materials, or other categories, organic ones have a high instability if they are made to work at high temperatures because of the bonds that make up the material that are of covalent type.

3.1 ORGANIC PARAFFINIC MATERIALS

Paraffin waxes are the most used among phase change organic materials. It belongs to the family of hydrocarbons, mainly alkanes, characterized by chains with more than 20 carbon atoms. They are characterized by large phase change properties and have excellent chemical stability in contact with other different materials. To avoid further dispersion during phase change, it is necessary to enclose the paraffin with high thermal conductivity materials. This encapsulation, however, if it were installed inside the opaque envelope of a building, would make the entire wall much weaker if subjected to mechanical stress. [24]



Figure 19 Enthalpy of fusion variation belong to temperature of application [25]

As can be seen from the graph in figure 19, the paraffin have a very wide operating temperature range, comparable to that of the hydrated salts. However, what is observed is also the amount of fusion enthalpy, which has much lower values than other phase change materials.

In addition there are various types of paraffin, and this is due to the amount of carbon atoms inside the chain.

Carbon Number Melting Point (°C)		Latent Heat (kJ/kg)	
14	4.5 - 5.6	231	
15	10	207	
16	18.2	238	
17	22	215	
18	28.2	245	
19	31.9	222	
20	37	247	
21	41	215	
22	44	249	
23	47	234	
24	51	255	
	Carbon Number 14 15 16 17 18 19 20 21 22 23 24	Carbon Number Melting Point (°C) 14 4.5 - 5.6 15 10 16 18.2 17 22 18 28.2 19 31.9 21 41 22 44 23 47 24 51	

Figure 20 Various types of paraffin [26]

As can be seen from the previous table in figure 20, the variation in the amount of carbon atoms, it is possible to obtain a large quantity of paraffin waxes with different melting temperatures and latent heat. In fact, as the numbers of carbon atoms increase, the melting temperature increases. While the variation of latent heat of fusion depends on the amount of carbon atoms within the chain, but does not depend on their increase.

As mentioned previously, the paraffin has a temperature range, which is around 20 to 70 °C, which would then allow it to be used for a wide range of energy applications. However, paraffin, unfortunately, has a very low conductivity of about 0.2 $\frac{W}{mK}$, thus making the phase-change accumulation phase, for each energy application, less performing.

This unfavourable condition would result in a reduction in the amount of heat transmitted in the medium and would increase the melting time of the material.

Numerous studies have been carried out in such a way as to increase thermal conductivity. A first test carried out was that of the paraffin encapsulation with a high conductivity material, as already mentioned above, or installing the organic material inside a matrix made of a material

with high thermal conductivity or installing a wing around the tube in which the fluid passes, so as to increase the heat exchange surface.

Finally, a very interesting study carried out by Whiffen and Riffat [27] would consist in mixing the paraffin with a metallic powder. In this case, the material used expanded graphite (EG).



Figure 21 Temperature variation between generic paraffin and paraffin mixed with EG [27]

The test was carried out because a considerable difference in level was determined from the standpoint of duration between the charge and discharge phase. In fact, the charging phase had a longer life than the solidification process of the phase change material.

As can be seen from the graph, the mixture of paraffin and expanded graphite powder allowed to reduce the time during the charging phase. This observation was determined by the simple fact that the mixture reaches the melting temperature in a shorter time than the duration of the simple paraffin was charge phase.

The test determined that having a good percentage of mixed metal powder inside the paraffin would increase the thermal conductivity, low thermal dispersions would be obtained, chemical stability, excellent compatibility and would keep the density of the material low.

In fact, the other characteristics that make the paraffin unique, as we will see for the other organic materials, is that in addition to having good thermal qualities, and its flammability, its non toxicity and even the failure to achieve the undercooling, which we obtain in the phase of discharge and crystallization of an inorganic phase change material.

From what has been found, therefore, is that paraffin is an excellent competitor in the field of phase change materials.

Despite having rather low thermal characteristics, compared to other materials, modest costs, which are between 0.5 and $10 \frac{\epsilon}{kg}$, paraffin waxes can be found as a phase change in thermal storage systems obtaining excellent results. [27]

3.2 NON-PARAFFINIC ORGANIC MATERIALS

Non-paraffinic organic materials are a very interesting alternative to generic paraffin waxes. These components are more available than generic organic materials.

Among the non-paraffinic organic materials, most of the studies have been carried out on fatty acids.

Fatty acids are mainly composed of a long chain of carbon atoms and can be divided into two categories: saturated fats and unsaturated fats.



Figure 22 Chemical difference between saturated and unsaturated fatty acids [28]

As can be seen from the figure 22, the characteristic that differentiates saturated and unsaturated fatty acids is the link between the carbon atoms within the chain. In fact, in saturated fatty acids, the carbon atoms are connected to each other by single bonds while the unsaturated ones have double bonds inside their structure.

This sharp distinction also makes numerous types of fatty acids differentiated mainly by the melting temperature.

FATTY ACIDS							
Saturated			Unsaturated				
Formula	Common	Melting	Formula	Formula Common			
	Name	Point		Name	Point		
CH ₃ (CH ₂) ₁₀	Lauric	45°C	CH ₃ (CH ₂) ₅ CH=CH(CH	Palmitoleic	0 °C		
CO ₂ H	acid		2)7CO2H	acid			
CH3(CH2)12	Myristic	55°C	CH ₃ (CH ₂) ₇ CH=CH(CH	CH ₃ (CH ₂) ₇ CH=CH(CH Oleic acid			
CO ₂ H	acid		2)7CO ₂ H				
CH3(CH2)14	Palmitic	63°C	CH ₃ (CH ₂) ₄ CH=CHCH ₂ Linoleic		-5 °C		
CO ₂ H	acid		CH=CH(CH ₂) ₇ CO ₂ H	acid			
CH3(CH2)16	Stearic	69°C	CH ₃ CH ₂ CH=CHCH ₂ C Linolenic		-11 °C		
CO ₂ H	acid		H=CHCH ₂ CH=CH(CH acid				
			2)7CO2H				
CH3(CH2)18	Arachidic	76°C	CH ₃ (CH ₂) ₄ (CH=CHCH	Arachidonic	-49 °C		
CO ₂ H	acid		2)4(CH2)2CO2H	acid			

From the previous table [29] it is possible to notice that in saturated fatty acids the melting temperature increases as the CH₂ group increases, while the unsaturated fatty acids are mainly exploited in the applications that work at cryogenic temperatures.

Fatty acids are very important because they have higher thermodynamic properties than other PCMs such as fusion congruence, good chemical stability, non-toxicity that allow their use for a large number of passive solar heating applications. [30]

These materials, in their liquid phase, have a surface tension of the order $2-3 \cdot 10^{-4} \frac{N}{cm}$ which is high enough to be retained in the structure of the host material.

As can be seen from the table in figure 23, the increase not only affects temperatures, but also other thermodynamic characteristics. In fact, the increase in the quantity of carbon atoms belonging to the main chain of the compound is directly proportional to the increase in melting temperature but inversely proportional to the amount of latent heat of fusion.

While, as regards the specific heat at constant pressure, its increase does not depend fundamentally on the number of carbon atoms of fatty acid, but its increase depends on the state of aggregation of the molecules.

Fatty acid	Chemical formula	Latent heat (J/g)	Measured phase transition temp.(°C)	Specific heat (J/g °C)	
				C _{p,s}	C _{p,1}
Stearic Acid (> 90%)	C ₁₇ H ₃₅ COOH				
(> 40% Stearic and $> 40%$ Palmitic acid)		174.6	53.8	1.6	2.2
Palmitic acid (95%)	C ₁₅ H ₃₁ COOH	197.9	59.9	1.9	2.8
Myristic acid (95%)	C ₁₃ H ₂₇ COOH	192.0	53.8	1.7	2.4
Lauric acid (97%)	C ₁₁ H ₂₃ COOH	211.6	42.6	1.7	2.3

Figure 23 Thermal properties for different fatty acids [31]

In fact, the specific heat increases in the melting phase of the material.

In general, the specific heat at constant heat will have values ranging from 1.6 to $2.8 \frac{J}{g^{\circ}c}$, which depends not only on the type of material but also on the state of the material.

A further characteristic of fatty acids is that during the phase change phase, small variations in volume may occur and furthermore, during the phase of discharge and therefore of heat transfer of the fatty acid to the fluid, no phenomenon occurs below cooling, which would make the use of the material very advantageous.

For the carboxylic group, fatty acid based PCMs are chemically and thermally stable, with low corrosion and non-toxic activity.

The raw materials of fatty acids derive from renewable vegetable and animal sources, which would therefore ensure a continuous source of non-polluting supply.

The fatty acid based PCM can be produced by the following procedures:

- Triglycerides present in nature;
- Hydrate of triglyceride acids and their mixtures;
- Esters of fatty acids and triglycerides present in nature;
- Triglyceride products synthesized by hydrogenation and fractionation;
- Synthesized triglyceride products using isomerization and cis-trans fractionation;
- Derived fatty acid derivatives that have the desired temperatures for the freezing point;
- Hydrates of refined fatty acids which have the desired temperatures for the freezing point;

 Prepared mixtures essentially produced from any of the previous processing approaches with other chemicals to produce eutectic compositions with the desired temperature range for the freezing point. [30]

3.3 NON-PARAFFINIC ORGANIC MATERIAL EXAMINATED

As noted in the previous paragraph, non-paraffinic organic materials having good thermodynamic characteristics, they can be used for a wide range of energy production systems such as phase change storage materials.

Having already anticipated that, these materials will be used predominantly for the energy storage of renewable source systems, most of the investment costs will be used for the energy production system therefore trying to save for storage costs.

In addition, that is why the studies focused on low cost materials, for their easy availability, such as organic materials.

In this case, it has been noted that non-paraffinic organic materials have had excellent results and are also preferred to other PCMs because of their low cost.

The study carried out is that of being able to lower costs by trying to exploit waste materials as phase change accumulation materials.

In this case, after having carried out some research, we tried to deepen the study on lard, butter and meat fat produced by a post-cooking process.

These three materials are taken for verifying their feasibility of use in the field of thermal storage and finally comparing them with a generic organic material with phase change as paraffin wax.

3.3.1 LARD

Lard is a material used for food obtained through the fusion of elements present in the adipose tissue of the pig. It is commonly used for frying or kneading.

Together with butter, it was decided to use this material for phase-change thermal storage. Lard consists of 97.28% fat, 0.003% protein, 0.005% water and the remainder of vitamins and minerals. For the energetic characterization of the lard, it has been found very difficult in the research of the thermodynamic properties since the component is almost never used for scientific purposes. Through research the found thermodynamic properties are density, specific heat (in liquid and solid phase), thermal conductivity and melting temperature.

As far as density is concerned, at 15 °C, it does not have precise values and this is due to the percentage of components and the type of processing.

In fact the value goes from 0.9140 to 0.9430 g/ml and then for the simulation phase a medium value will be used to simplify the data recording process.[32]

The specific heat assumes values equal to $1.3 \frac{kJ}{kgK}$ in the solid phase and $2.26 \frac{kJ}{kgK}$ in the liquid phase, values that are appropriate for the study examined.[33]

Through the study carried out by Lentz in 1961 [34], it is certified that the thermal conductivity of the lard takes a value equal to $0.215 \frac{W}{mK}$ at 3 °C while $0.218 \frac{W}{mK}$ at -15 °C. This means that, even in this case, the thermal conductivity varies with temperature changes.

In this case, the thermal conductivity is inversely proportional to the temperature and to have values close to the real ones, during the simulation, through these two values we will try to draw a weighting curve.

Finally, the melt temperature instead assumes values of 41 °C, which allows to be able to advance assumptions of feasibility of use of the material for a phase change thermal storage system.[35]

3.3.2 BUTTER

Butter is a derivative of milk and consists mainly of water for 15.11%, of fats for a good 83.59%, of proteins for 1.18% and finally of 0.12% of other waste.[36]

The main composition of the butter is mostly fatty acids and this makes it difficult to calculate its thermodynamic characteristics.

From previous studies, it has been verified that the density of butter, compared to other milk derivatives, is much lower. This is a quantity of raw materials that distinguishes butter from other milk derivatives.
Product	Density (kg/m ³)	pH	Total solids content (%)
Butter	942.3	4.52	84.89
Cheddar Cheese	1102.0	5.15	64.00
Hamburger Cheese	1114.0	5.60	59.00
Old Kashkaval Cheese	1117.0	5.25	59.00
Tulum Cheese	1110.0	5.21	59.00
Fresh Kashkaval Cheese	1181.7	5.16	56.21
Mozzarella Cheese	1062.4	5.33	55.65
Buffet Kashkaval Cheese	960.9	5.11	50.16
Fresh Cream Cheese	1014.1	5.38	43.68
Labne	1084.7	4.36	30.87
Low Fat Labne	1085.2	4.41	25.35
Spreadable Cheese	823.8	5.78	39.40
Strained Yogurt	972.1	4.51	25.77
Light Yogurt	1033.1	4.20	18.05
Pasteurized Yogurt	1034.8	4.10	17.52
Extra Light Yogurt	1024.5	4.20	13.19

Figure 24 Density of dairy products [36]

As far as the melting temperature is concerned, the complex composition of the butter, consisting of many fatty acids, makes its calculation difficult.

Common Name	Formula	Melting Point			
Soluble volatile fatty acids					
Acetic acid	C ₂ H ₄ O ₂	-16 °C			
Propionic acid	C ₃ H ₆ O ₂	-20 °C			
Butyric acid	C ₄ H ₈ O ₂	-8 °C			
Insoluble	volatile fatty aci	ds			
Caproic acid	C ₆ H ₁₂ O ₂	+3 °C			
Caprilic acid	$C_8H_{16}O_2$	+16 °C			
Capric acid	$C_{10}H_{20}O_2$	+30 °C			
Lauric acid	$C_{18}H_{36}O_2$	+42 °C			
Fixe	d fatty acids				
Myristic acid	$C_{14}H_{28}O_2$	+54 °C			
Palmitic acid	$C_{16}H_{32}O_2$	+62 °C			
Stearic acid	C ₁₈ H ₃₆ O ₂	+70 °C			
Unsatur	ated fatty acids				
Palmitoleic acid	$C_{16}H_{30}O_2$	+1 °C			
Oleic acid (cis)	$C_{18}H_{34}O_2$	+16 °C			
Vaccenic acid (trans)	$C_{18}H_{34}O_2$	+43 °C			
Polyunsat	urated fatty aci	ds			
Linoleic acid	$C_{18}H_{32}O_2$	+4 °C			

Figure 25 Melting points of single components of dairy products [37]

It is possible to notice, from the previous table in figure 25, the fatty acids that make up milk fat, that is the main component from which butter and other derivatives come from, all have different temperatures.

To simplify the study, on average the butter has a melting temperature that is between 32 and 35 °C until it has completely melted the material at 40 °C.[37]

foods	Т _т (°С)	<i>Т_b</i> (°С)	L _f (kJ/kg)	L_v (kJ/kg)
butter	32~35			
lard	41			
margarine, table	34~37			
margarine, bakery	38~43			
oil, cocoa butter	34			
oil, coconut	24			
oil, corn	-20? -15?			
oil, olive	-6			
oil, palm	~35			
oil, peanut	3			
oil, soya	-16? -13?			
shortening, vegetable	44~50			
sugar, fructose	104			
sugar, glucose	146			
sugar, sucrose	186			

Figure 26 Melting temperature for some foods [35]

As for thermal conductivity, its determination remains very complex to solve. As the butter, as well as other organic materials, consisting of many elements, for the calculation of thermal conductivity, and other thermodynamic characteristics, studies have been carried out with the aim of making it easier to calculate.

Thermal Property	Food Component	Thermal Property Model
Thermal Conductivity W/(m·K)	r, Protein Fat Carbohydrate Fiber Ash	$ \begin{split} k &= 1.7881 \times 10^{-1} + 1.1958 \times 10^{-3}t - 2.7178 \times 10^{-6}t^2 \\ k &= 1.8071 \times 10^{-1} - 2.7604 \times 10^{-3}t - 1.7749 \times 10^{-7}t^2 \\ k &= 2.0141 \times 10^{-1} + 1.3874 \times 10^{-3}t - 4.3312 \times 10^{-6}t^2 \\ k &= 1.8331 \times 10^{-1} + 1.2497 \times 10^{-3}t - 3.1683 \times 10^{-6}t^2 \\ k &= 3.2962 \times 10^{-1} + 1.4011 \times 10^{-3}t - 2.9069 \times 10^{-6}t^2 \end{split} $
Thermal Diffusivity, m ² /s	Protein Fat Carbohydrate Fiber Ash	$ \begin{split} \alpha &= 6.8714 \times 10^{-8} + 4.7578 \times 10^{-10}t - 1.4646 \times 10^{-12}t^2 \\ \alpha &= 9.8777 \times 10^{-8} - 1.2569 \times 10^{-10}t - 3.8286 \times 10^{-14}t^2 \\ \alpha &= 8.0842 \times 10^{-8} + 5.3052 \times 10^{-10}t - 2.3218 \times 10^{-12}t^2 \\ \alpha &= 7.3976 \times 10^{-8} + 5.1902 \times 10^{-10}t - 2.2202 \times 10^{-12}t^2 \\ \alpha &= 1.2461 \times 10^{-7} + 3.7321 \times 10^{-10}t - 1.2244 \times 10^{-12}t^2 \end{split} $
Density, kg/m ³	Protein Fat Carbohydrate Fiber Ash	$\begin{split} \rho &= 1.3299 \times 10^3 - 5.1840 \times 10^{-1}t \\ \rho &= 9.2559 \times 10^2 - 4.1757 \times 10^{-1}t \\ \rho &= 1.5991 \times 10^3 - 3.1046 \times 10^{-1}t \\ \rho &= 1.3115 \times 10^3 - 3.6589 \times 10^{-1}t \\ \rho &= 2.4238 \times 10^3 - 2.8063 \times 10^{-1}t \end{split}$
Specific Heat, J/(kg·K)	Protein Fat Carbohydrate Fiber Ash	$\begin{split} c_p &= 2.0082 \times 10^3 + 1.2089t - 1.3129 \times 10^{-3}t^2 \\ c_p &= 1.9842 \times 10^3 + 1.4733t - 4.8008 \times 10^{-3}t^2 \\ c_p &= 1.5488 \times 10^3 + 1.9625t - 5.9399 \times 10^{-3}t^2 \\ c_p &= 1.8459 \times 10^3 + 1.8306t - 4.6509 \times 10^{-3}t^2 \\ c_p &= 1.0926 \times 10^3 + 1.8896t - 3.6817 \times 10^{-3}t^2 \end{split}$

Figure 27 Thermal properties for each food component [38]

A very interesting study was made by Brian A. Fricke and Bryan R. Becker [38], and it was interesting to note that the characteristics of an organic material not only depend on the composition of the element taken into consideration, but also on the temperature.

Obviously every organic material has its own composition and quantity of proteins, fats, fibers and other materials, and therefore for the calculation of the thermal conductivity the formula $k = \sum x_i^{\nu} k_i$ has been used, where x_i^{ν} corresponds to the volumetric fraction of each individual component of the material and k_i its thermal conductivity.

Product	k (measured	l) (W/m K)	Standard de	eviation (W/m K)	k (calculated by E_{π} (2) at 15%
	15°C	30°C	15°C	30°C	(W/m K)
Butter	0.227	0.233	0.013	0.009	0.236
Cheddar Cheese	0.345	0.351	0.010	0.001	0.346
Hamburger Cheese	0.381	0.398	0.009	0.005	0.377
Old Kashkaval Cheese	0.368	0.384	0.008	0.007	0.370
Tulum Cheese	0.379	0.377	0.006	0.005	0.368
Fresh Kashkaval Cheese	0.403	0.403	0.009	0.002	0.384
Mozzarella Cheese	0.383	0.380	0.003	0.005	0.384
Buffet Kashkaval Cheese	0.406	0.409	0.003	0.001	0.413
Fresh Cream Cheese	0.433	0.434	0.005	0.006	0.432
Labne	0.486	0.463	0.007	0.009	0.473
Low Fat Labne	0.548	0.542	0.025	0.010	0.506
Spreadable Cheese	0.476	0.494	0.003	0.016	0.454
Strained Yogurt	0.540	0.539	0.008	0.012	0.510
Light Yogurt	0.571	0.583	0.005	0.004	0.545
Pasteurized Yogurt	0.571	0.593	0.007	0.022	0.543
Extra Light Yogurt	0.584	0.596	0.002	0.003	0.560

Figure 28 Thermal conductivity of dairy products [36]

Through these studies, the interpretation of the calculation of thermal conductivity has led to further theories that made it difficult to calculate and that is why we have tried to simplify the problem by using the result obtained by I.H. Tavman and S. Tavman [36] where the thermal conductivity assumes a value of 0.227 $\frac{W}{mK}$ at 15 °C and 0.233 $\frac{W}{mK}$ at 30 °C.

As can be seen from the table, the thermal conductivity of the butter has a much lower value than the other milk derivatives, which however more or less assumes the same tendency to vary the temperature.

Moreover, thanks to the same study, the value of the density of butter equal to 642.3 $\frac{kg}{m^3}$ is assumed for simplicity.

The same reasoning was made at the specific heat and in this case reference was made to the study carried out by Hammer and Johnson in "The specific heat of milk and milk derivate" [39], and we have reached the conclusion described in the following table.

Specific heat $\frac{J}{kgK}$					
	At 0 °C	At 15 °C	At 40°C	At 60°C	
Whey	0.978	0.976	0.974	0.972	
Skim Milk	0.940	0.943	0.952	0.963	
Whole Milk	0.920	0.938	0.930	0.918	
15% Cream	0.750	0.928	0.899	0.900	
20% Cream	0.723	0.940	0.880	0.886	
30% Cream	0.673	0.983	0.852	0.860	
45% Cream	0.606	1.016	0.787	0.793	
60% Cream	0.560	1.053	0.721	0.730	
Butter	0.512	0.527	0.556	0.580	
Butter Fat	0.445	0.467	0.500	0.530	

Figure 29 Specific heat of dairy products [39]

From the table it is observed that the specific heat of the butter takes on low values compared to the other derivatives and therefore the amount of heat that will serve to raise a Kelvin degree one kilogram of butter will be much lower than the amount of heat that is needed for the others derivatives.

Furthermore, the growth in the quantity of specific heat is directly proportional to the increase in temperature, which in some dairy products this correlation between specific heat and temperature is not obtainable.

In other cases the specific heat assumes a value of $1.42 \frac{kJ}{kgK}$ in the solid phase and $2.72 \frac{kJ}{kgK}$ in the liquid phase.[33]

The butter from a first observation has good thermodynamic performance and therefore has been considered for use as a phase change material for thermal storage systems.

The material not only has excellent thermodynamic characteristics but is easily available, non toxic, does not corrode in contact with other materials and is economical.

Its availability is due to the high use of butter in the food chain, which is why we will investigate the possibility of being able to use waste for a phase change thermal system for space heating or domestic hot water.

3.3.3 MEAT FAT

As third material is taken in consideration, meat fat obtained by a post-cooking process.

This material it is not used as thermal storage process, so it was very difficult research all its thermal characteristics.

First of all, meat fat is principally composed by saturated fat ad by this material are prepared other products, as for example lard.

Its low utilization in thermal field, has made the determination of some thermodynamic characteristics very difficult. In fact, it was possible deriving density, that has a value equal to $930 \frac{kg}{m^3}$, and thermal conductivity that has a value equal to $0.23 \frac{W}{mK}$. [34]

While for the specific heat, it was used the same of the lard, for its similar composition.

At the end, also for the melting temperature, no real scientific correspondence has been found, so for simplicity it was adopted the same melting temperature of the lard, 41°C.

For the others thermal elements, not used for our study, is not done a deeper survey.

3.3.4 PARAFFINIC WAX

As already mentioned above, unlike the three previous compounds, paraffin wax is one of the most used among phase change organic materials for thermal storage systems.

Being the most exploited, numerous studies have been carried out that have allowed to give a well defined energetic characterization.

In the previous paragraphs it has been shown how the thermodynamic properties of paraffin depends a lot on its chemical composition. In fact, paraffin is an organic component characterized mainly by a long carbon chain. The variation in length of the main chain will affect the properties of the compound.

Micro/nano EPCM	Solid-liquid phase change (melting) temperature (°C)	Latent heat of melting (J/g)	Liquid-solid phase change (freezing) temperature (°C)	Latent heat of freezing (J/g)
n-Heptadecane (C17)	21.36	216.21	21.36	-213.96
n-Octadecane (C18)	27.79	226.17	24.58	-223.96
n-Nonadecane (C19)	31.45	230.75	31.45	-223.80
n-Eicosane (C20)	36.17	276.41	32.92	-268.38
n-Tetracosane (C24)	50.09	275.02	50.09	-243.46
(C17-C24) (90-10%)	19.24	171.14	20.61	-167.52
(C19-C18) (5-95%)	25.15	180.28	21.12	-175.14
(C19-C24) (95-5%)	32.20	187.90	30.87	-186.87
(C20-C24) (90-10%)	35.80	265.60	34.80	-255.60

Figure 30 Variation of thermal properties of paraffinic wax which depends by the number of carbon atoms into the chain [24]

From the study carried out by Sari, Alkan and Bilgin, it was determined how the temperature and the latent heat not only depends on the length of the chain of carbon atoms but also if we are in the process of melting or solidifying the compound. [24]

With regard to the specific heat for simplicity, it maintains an almost constant value of $2.13 \frac{kJ}{kgK}$, during the process it accumulates and independently of the quantity of carbon atoms that make up the material. [40]

The conductivity of the paraffin wax takes on a value equal to $0.25 \frac{W}{mK}$ at a temperature of 25 °C and as you can see, although it is the most used material among those with phase change for the thermal storage systems, the paraffin it has a thermal conductivity very similar to the other two organic materials that will be examined later. [41]

What will be verified in the next chapter is if the lard and butter can be excellent substitutes as accumulation materials and you can have energy benefits, in addition to the economic ones, to the detriment of the classic paraffin wax.

3.4 DSC ANALYSIS

To determine in more detail the energy characterization of the materials that will be taken into consideration, it is considered to undertake the analysis DSC (Differential Scanner Calorimetry).

With the help of the Department of Applied Science and Technology of the Polytechnic of Turin, machinery was used to determine the thermodynamic properties of phase change organic materials.

Differential scanning calorimetry allows direct measurement of the amount of heat emitted or absorbed by the sample through a compensation mechanism, based on maintaining the thermal equilibrium (temperature equality) between sample and reference.

Sample and reference are inserted into two separate cells; their temperature is monitored by means of two thermocouples in contact with the crucibles containing them.

A first electric circuit determines the heating of both cells on the basis of the average measured temperature; this heating is programmed with the temperature growth rate chosen as desired in the interval between 1 and 100 °C per minute.



Figure 31 DSC Analysis machine



Figure 32 Schematic diagram of the measuring cell and of the electric circuits of heating and compensation of the purchased or sold heat of a DSC equipment. On the right, is shown the specimen inserted inside the machine.

A second circuit warms the sample and reference in a differentiated manner, keeping the same at the same temperature even in the presence of exothermic or endothermic phenomena. The amount of energy supplied by the compensation circuit, when these phenomena occur, is equal to the amount of heat involved in the transformation undergone by the sample.



Figure 33 Typical DSC curve [42]

The obtained DSC curve represents the differential heat delivery rate as a function of time or of the average temperature of the system. The maximum sensitivity of the instrument is 0.1 mcal/s.

The speed at which the system compensates for example the heat absorbed during a sample transformation (dH/dt) depends on both the programmed heating rate (dT_p/dt) and the thermal resistance R_0 according to the equation:

$$\frac{dH}{dt} = \frac{1}{R_0} \bullet \frac{dT_p}{dt}$$
(1) T_p = programmed temperature; R₀ = thermal resistance of the system

Therefore, the peaks will grow more or less rapidly depending on these parameters: clearer peaks will be obtained with a higher programmed heating rate and when the gaseous atmosphere in the measuring cell allows faster conduction of heat.

If the heating rate is high, the sample may be in a condition of greater thermodynamic instability, which requires a greater amount of energy consumed in the unit of time to complete the transformation. If the thermal resistance of the system is large, the sample can only acquire energy slowly. Even if the above experimental parameters influence the shape of the peak, the underlying area will be however independent of the experimental conditions adopted, therefore in any case the instrument will provide a correct measurement of the heat involved.

The main limits of the differential scanning calorimetry are in the application temperature range, which extends only between -150 °C and about 700 °C. These limits, in particular with reference to the maximum temperature attainable, are instrumental in nature, and therefore difficult to overcome.

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The determination of the onset of a phenomenon consists in the evaluation of the temperature of the system in correspondence of which a deflection of the baseline is observed.



Figure 34 Various criteria with which the baseline can be drawn in a calorimetric pattern. [42]

Modern tools allow this operation to be carried out easily, graphically processing the thermogram using a personal computer that has a dedicated software.

The measured temperature values for a precise phenomenon during a calorimetric test depend on numerous experimental parameters:

- Position of the crucible on the base of the sample holder;
- Quantity and type of material in the crucible, i.e. thermal capacity of the sample;
- Geometric form of the sample, i.e. ability to receive or transfer heat to the crucible;
- Emissivity of the sample, or capacity to yield heat by irradiation,
- Heating speed with which the test is conducted;
- Sensitivity of thermocouples at various temperatures.

In order to minimize experimental errors in temperature measurement, it is advisable to conduct calibrations with appropriate standards, adopting the same experimental conditions that will then be used in the measurement.

The execution of the aforementioned calibration procedures does not in any way exempt from the adoption of some measures during the measurement: standardize the position of the crucible, operate with a few milligrams of sample substance, close the crucible with a lid to reduce the emissivity of the sample.

Since the response of the measurement thermocouple varies with temperature changes, a standardization procedure should be performed throughout the range of temperatures of interest, obtaining the necessary correction factor (i.e. a correction curve) for each temperature. This type of correction is carried out by the management software of the most modern tools. In this case it is sufficient to make calibrations with few standards that have a known transition temperature.

The most update instruments even include the use of a single standard, entrusting the software with temperature correction, even at temperatures very different from those in which the standard presents a transformation.

However, it is good practice to use two calibration standards to minimize the measurement error in a wide temperature range, or, in the case of very precise measurements, use a calibration standard that presents a transition near the temperature value at which check the phenomenon that you intend to study. Calibration is normally carried out by high purity metals with known melting temperature.

The same DSC instrument allows measuring the specific heat of substances using the procedure briefly described below.

$$\frac{dH}{dt} = m \cdot C_p \cdot \frac{dT_p}{dt}$$
(2)

where:

dH/dt = heat supplied in the unit of time;

m = mass of the sample;

 C_p = specific heat of the sample;

 $dT_p/dt = programmed heating rate.$

Having determined, through the previous analysis, the variation of enthalpy over time, the variation of the temperature over time and the mass of the sample, it is possible to determine the specific heat of the material at constant pressure.

At first, a test is carried out with the crucibles (in which the sample and reference are normally placed) empty, using the thermal cycle represented in the lower part of the follow figure. Initially a baseline is recorded keeping the instrument in isothermal conditions minimum temperature of the interval in which the specific heat is to be studied, then the temperature is

increased up to the maximum value of this range of temperatures of interest, finally a new base line is obtained with the isothermal treatment at the final temperature.

The baseline in the considered range will be obtained by interpolating these two baselines. Two DSC measurements are then performed, increasing the temperature in a linear fashion with the time in the range of interest: the first measurement will be carried out by placing the test substance in the crucible (sample site), the second will be done by placing a material in the crucible which is well known the specific heat at various temperatures (for example sapphire, or an alumina single crystal). These two curves will be placed above the baseline since it is necessary to provide heat to heat both the sample and the sapphire.



Figure 35 Calculation of the specific heat

These quantities of heat are represented in Figure 35 (at any temperature) by the difference between the ordinate of the curve in question and the ordinate of the baseline; for example they (at a certain temperature shown in the figure) assume the values of Y 'and Y respectively for the sapphire and for the sample under examination. In both cases there are reports:

$$Y = \mathbf{m} \bullet \mathbf{Cp} \bullet \frac{dT_p}{dt} (3)$$
$$Y' = \mathbf{m'} \bullet \mathbf{Cp'} \bullet \frac{dT_p}{dt} (4)$$

that comparing member to member provide the relationship:

$$\frac{C_p}{C'_p} = \frac{Y \cdot m'}{Y' \cdot m}$$
(5)

Where m and m 'are the sample and sapphire masses respectively. Using the previous formula it is possible to obtain the specific heat value of the test substance (Cp). This operation can be carried out for each temperature in the considered range.

4. EXPERIMENTAL PHASE

As already announced in the previous chapter, the purpose of our study will be to be able to verify an energy feasibility of organic waste materials from the food supply chain, such as butter and lard, and compare them with a generic organic material used in the storage system like paraffin.

The experimentation takes place on two levels: an experimental one carried out in the laboratory and a simulation programmed through the COMSOL Multiphysics 5.3a software.

Furthermore, the laboratory phase has been developed on several working steps, thus allowing more useful results to be obtained in order to then draw more truthful conclusions and more precise outcomes.

In fact, not only tests were carried out based on the type of material, but further studies were carried out on two types of storage systems.

These two systems are: one in scale in which materials of daily use have been used, and the latter has components that are much closer to the thermal storage system.

The first type of system aims to verify the thermodynamic feasibility of organic waste materials in comparison with the generic paraffin wax. The second type, on the other hand, aims to verify a possible replacement of organic waste materials with paraffin in the thermal storage system used mainly for heating domestic environments.

4.1 TESTS ON SMALL SYSTEM

Regarding the first type of tests carried out in the laboratory are mainly used daily materials in such a way to reduce costs in the preliminary phase of study. While for the measurement and data recording phase it was necessary to use simple thermocouples which, connected to a software, could be used to record the monitored data. Finally, the system has been reproduced on the simulation software, in order to have feedback and to verify if the results coincide or not with the values measured in the laboratory.

4.1.1 MATERIAL USED

The materials that were used for the first phase in the laboratory are:

- A polypropylene container, 15 cm deep, 7.3 cm high and 22.2 cm wide. The container also has a junction with a curvature of about 2 cm. Finally, the thickness of the container is almost uniform and is about 2 mm.
- A polypropylene container, measuring 10.7 cm in depth and width and 4 cm in height.
 Also in this case the container has a junction with a radius of curvature of about 2 cm.
 The thickness, as well as the larger container, is constant and is equal to 2 mm.
- An aluminium container, shaped like a truncated cone with a lower radius of 2.75 cm, a greater radius of 3.5 cm and a height of 3.8 cm. Despite being of different material, also in this case the thickness is equal to the other containers and is 2 mm.
- 5 thermocouples, which were used for detecting temperatures at various points in our system. 5 of these, 4 are of type N and one of type T.

In addition to the materials mentioned above, the study will be done for lard, butter, paraffin and fat in order to have a comparative analysis between the three compounds and as regards the insulation layer the wood sawdust has been chosen which will remain unchanged for the duration of the study in the laboratory.

For monitoring phase the SignalExpress software was used, which allows to record the temperature measured by the five thermocouples at each second and then the values are inserted in tables using the Excel program.

Finally, the heat source that will allow us to describe the phenomenon of phase change of the materials is the hot water that is previously heated through a very simple kitchen boiler.

Through the boiler the water must reach the temperature useful for the charge phase of the organic PCM and to monitor the temperature reached use a digital thermometer that shows the temperature from the display, to be able to remove the hot water from the boiler at the right temperature.

The preliminary phase to the recording of temperatures, is that of assembly that allows you to understand how to position the various components, but above all where to place the 5 thermocouples inside the system, so that based on its monitoring point you can understand which thermocouples will record higher temperatures than the others.

Furthermore, the assembly phase of the scale system will be similar for all three phase change compounds. The only variant will be the PCM inside one of the three containers.

4.1.2 ASSEMBLY PHASE

Before positioning the thermocouple, the weighing of the largest container was carried out, thus obtaining a value equal to 65 g.

Then the thermocouple is installed on the bottom of the container, which we will indicate as T0, fixing it with a very simple scotch tape.



Figure 36 Larger container with thermocouple T0 on the bottom

Subsequently, the weighing of the wood sawdust is carried out obtaining a value equal to 370 g and immediately after it is introduced into the container and positioned in such a way as to leave the space for the smaller container.

Regarding the thermodynamic properties of sawdust, reference was made to the tabulated values of the COMSOL Multiphysics 5.3a software.

In fact, the software allows, as we will see later, to select the material present in the database and to have already tabulated values. In this case, for sawdust, thermal conductivity values equal to $0.125 \frac{W}{mK}$, of specific heat equal to $1850 \frac{J}{kgK}$, while for density, being dependent on temperature, values will be obtained that will vary with temperature variation, but which however, it will have values that will be around $200 \frac{kg}{m^3}$ density. [43]

In order to have the most stable values possible in the monitoring phase in the laboratory, we tried to keep the weight of the sawdust unchanged.



Figure 37 Application of wood sawdust

After the phase of placing the sawdust inside the first container, the assembly phase continues with the installation of the thermocouple (T3), outside the second container, on the bottom and then facing the part of sawdust.



Figure 38 Smaller container with thermocouple T3 on the bottom, outside

In this case, for a better specification, also the polypropylene container was weighed obtaining a value equal to 22.5 g.

To avoid a possible poor temperature recording, also for the thermocouple T3 has been fixed on the bottom of the container with adhesive tape.

As you can see from the photo, the smallest container has had a good adherence to the space released inside the sawdust.

In such a way as to avoid as much heat loss as possible due to conduction since there will be many due to the simple fact that the entire system is exposed, from the top, outside.

The next step of the assembly phase is the insertion into the smaller container of the phase change material.

As can be seen from the figure 39, the material in this case is the lard, in which an additional thermocouple (T4) has also been applied to the bottom of the container, which will serve to monitor the PCM temperature.

Applying the lard there were numerous difficulties since the container tended to smear and made it more difficult to apply the adhesive tape for fixing the T3 thermocouple.

Although we found problems in the installation phase of the lard, we tried to keep the weight of the material unchanged in order to have a homogeneity in the monitoring phase and obtain more or less similar values.



Figure 39 PCM into the smaller container with thermocouple T4 for the bottom part

The weighing of the phase change material was carried out subsequently, obtaining a value of 200 g.

Subsequently, a further thermocouple (T1) was applied, which will mainly serve for recording the average or PCM environmental temperature.

Immediately afterwards, inside the container of the phase change material, the aluminium container in the form of a truncated cone was applied, which will serve for the insertion of hot water.



Figure 40 Last container of aluminium

As you can see from the image the last thermocouple (T2) has been applied for monitoring the cooling of the hot water inside the aluminium container.

Also for this last insertion, both the water and the aluminium container were weighed, obtaining respectively 73 g and 27 g of weight.

The water, as previously mentioned, comes first the boiler and then poured into the aluminium container.

To monitor the achievement of the correct water operating temperature, a digital thermocouple has been introduced with display inside the boiler.

To have more differentiations of the same problem, we poured the water inside the aluminium container at different temperatures so as to have different trends and be able to verify the behaviour of the material in phase change to various thermal stresses.

At the end of each recording, the water container is removed and the water is poured into the kettle, so as to avoid waste.

Subsequently, the assembly process was applied for the butter, which has a weight of 250 g.



Figure 41 Application of the butter inside the smaller container

Immediately after weighing and inserting into the butter container, thermocouples were introduced while maintaining the same arrangement for all tests and for all phase change materials.



Figure 42Application of the smaller container inside the whole system

Then, the same procedure is done for the meat fat. In fact is applied 250 g of fat into the smaller container and it was studied the temperature trend and the thermal exchange between hot water and organic compound.



Figure 43 Meat fat applied into the smaller container

Finally, as last process of the first step of temperature recording, it was applied paraffin wax into the smaller container, for having a complete comparative analysis between organic waste materials and a generic organic compound used for thermal storage.

In this case it is installed into the smaller container a paraffin wax with a weight of 140 g.



Figure 44 Paraffin wax into the smaller container

4.1.3 SIMULATION WITH COMSOL MULTIPHYSICS SOFTWARE

As already mentioned above, in addition to the experimental test carried out in the laboratory, the COMSOL Multiphysics 4.3a software was used to perform a comparative analysis between the data obtained in the laboratory and the results obtained from the software. The first phase is to build the 3D component, trying to make it as faithful as possible to reality.



Figure 45 Geometry of the system

As can be seen from the figure, first of all the figures are represented and then some partitions of the objects have been made, in such a way as to be able to divide the domains according to the various stratifications and not according to the geometric shapes.

The partition is mainly used for determining the individual materials, for the initial conditions and for determining the temperature trend of the individual PCM.

So the component is, therefore, represented in the following way.



Figure 46 Representation of the system

As can be seen from the figure, the centre of the reference system is placed at the centre and at the bottom.

Moreover, unlike what is presented in reality, the aluminium container in the shape of a truncated cone does not protrude since it is supposed, ideally, that the level of water and other materials coincides with the height of the truncated cone.

The next phase was that of determining the materials for each individual layer.



Figure 47 Material for each single layer

As for some materials like aluminium, water, sawdust and polypropylene, they are already present in the software database.

So at this stage we proceeded to select the layer and give it the type of material.

While for the PCM, in this case the lard, the material was created as new, attributing the energy characteristics found in the literature.

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	Densità	rho	930	kg/m³	Proprietà di base	
	Conducibilità termica	k_iso ; k	k(T)	W/(m·K)	Proprietà di base	

Figure 48 PCM settings



Figure 49 PCM layer

As can be seen from the figure above, as regards density, it is attributed in single value, while for the other two data, thermal conductivity and specific heat, we have more values as they vary with temperature.

And that's why curves were built by performing a data interpolation.

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318.15	2260		273.15	0.215

Figure 50 Interpolation of specific heat and thermal conductivity

And so the curves that have been created are represented in the following way.



Figure 51 Interpolation curves

The phase following the determination of materials for the individual materials is that of the introduction of the boundary conditions.

First of all we chose the type of physics that manifests itself within our system, which corresponds in this case to the transmission of heat.



Figure 52 Boundary conditions of the system

As can be seen from the figure, first of all it is determined for each domain and stratification that make up the system.

Then the domain that corresponds to the water is determined and the remaining ones are solid. Subsequently, this part of the physics also serves to determine the initial temperature of the individual domains.

Then for the water an initial temperature of 328.15 K was applied and for the remaining domains a value equal to 293.15 K.

The last step is to apply thermal insulation to the outer contour and to the faces on which the symmetry plane has been applied.



Figure 53 Thermal insulation



Figure 54 Part of the system exposed to the outside

The next phase of setting is that of the mesh that allows, through mathematical models, to manipulate the geometric and thermodynamic data.



Figure 55 Mesh applied on the system

As you can see from the figure, a thick and triangular mesh was applied to all the domains. The last phase corresponds to the introduction of a transitional study that will allow to start the thermodynamic transmission between the various domains and the external environment.

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	Impostazioni: Controllato dalla Fisica Salvare i campi di Output mostazioni: Tutto

Figure 56 Setting of the study

First of all, is adopted a transistor study used principally for recording the temperature variation during the thermal exchange.

As can be seen from the figure, the main modification applied in the study is the duration of the simulation and the time interval for data and temperature acquisition at each time step. It was decided to set up the study with a duration of 5400 s with a time interval of 100 s.

After that, the same procedure is applied for all materials. The only different is the modification of the PCM thermal characteristics.

In fact, for the other three materials, butter, fat and paraffin wax, specific modifications have been applied to density, thermal conductivity and specific heat.

In particular, regarding for fat, is applied an interpolation for the specific heat, that is equal to the specific heat of the lard, while for the other two thermal properties, is applied a specific datum.

Also for butter is used an interpolation, in this case for the thermal conductivity, while for the other properties is applied a single number.

For the paraffin wax, ate the end, for all three thermal properties are been written, for an easier simulation, single numbers.

4.2 EXPERIMENTATION IN SCALE

The next phase is the scale reproduction of a domestic storage system.

The experiment is divided into two phases, that of charge and discharge of the phase change material.

The main purpose is to be able to check the duration of the two phases to which the organic component is subjected. Especially during the discharge phase, it will be possible to observe and record the temperature trend of the material and determine its thermal inertia.

In this case, to determine the potential of phase change materials, we will not only use the four materials of the previous experimental phase, but we will also carry out a vacuum test.

4.2.1 MATERIAL USED

Unlike phase change materials, which will remain the same for this experimental phase, the components used to construct the scale system and the position of the thermocouples are different.

First of all, the components used to define the stratigraphy of the thermal storage system are:

- A cylindrical polypropylene container with a diameter of 25.5 cm, a depth of 26 cm and a thickness of 2 mm. In this case the container was weighed obtaining a value equal to 323 g. This container will include the insulation layer and other smaller containers.
- A cylindrical polypropylene container with a diameter of 16 cm, a depth of 11.5 cm and a thickness of 2 mm. The container has been previously weighed obtaining a value of 130 g. This second container will comprise the amount of PCM to be heated and the water container.
- A cylindrical aluminium container with a diameter of 7.5 cm, depth of 11 cm and a thickness of 1 mm. The container was previously weighed obtaining a value of 47.4 g. This last container serves to keep the water in a rigid volume avoiding mass losses.
- A temperature regulator, used to heat the water and maintain its constant temperature throughout the heat exchange process. This instrument is connected to a resistance band

of 500 W, which will serve to heat the water, and to a thermocouple that will not only record the temperature for data analysis but also to adjust the strength of the resistance.

- 4 N-type thermocouples, used for recording temperatures during the process and for the subsequent data analysis phase.

As already mentioned above, with regard to the materials used for the heat exchange phase, the following were used:

- Lard;
- Butter;
- Paraffinic wax;
- Meat fat obtained from a previous cooking phase;
- Water;
- Wood sawdust;

Unlike previous phases, you will not use the kitchen boiler to heat the water, as you will use the resistance and the thermocouple inside the water to record its temperature trend but we will base the thermocouple connected to the temperature controller.

As previously done, the assembly phase will be similar for all components, the change will be made only in the substitution of a phase change material with another.

4.2.2 ASSEMBLY PHASE

The first assembly phase is that of assembling the first thermocouple, indicated as T0, inside the first larger container and positioning it along the side surface.

Moreover, as can be seen from the figure 57, sawdust has been positioned on the bottom of the container, so as to avoid thermal dispersions even downwards.



Figure 57 Thermocouple T0 inside the first container

Subsequently, the second container that was filled with the phase change material was introduced inside, in this case the lard.



Figure 58 Thermocouple T2 inside the second container

As can be seen from the figure, a thermocouple, T2, has been positioned on the inner edge of the PCM container, as it will allow to record the temperature.

Based on this positioning of the thermocouple and the behaviour of the material melting, it has been determined that the T2 thermocouple will record the minimum temperature of the phase change material.

From the figure, it is possible to notice that the PCM has been positioned on the bottom and on the edges of the container, so as to be able to leave the space for the introduction of the water container.

The phase change material was weighed before its use, thus reaching a value of 1125 g. The next phase consists in positioning the water container. First of all, the container was filled with water and with the aid of the scale a value of 342 g was reached while the container itself had a weight equal to 47.4 g.

After that, the container was closed by a simple adhesive tape, in order to avoid water leakage during assembly or during the replacement phase of the PCM.



Figure 59 Container of water with adhesive tape

The thermocouple is applied to the inner contour of the water container. The recorded temperature is used by the temperature regulator to moderate the strength of the resistance tape.



Figure 60 Container of water with resistance tape

As can be seen from the figure, the container with the resistance band is contained by a plastic bag, so that the resistance does not come into contact with the PCM.

Then a thermocouple was applied to the bag, indicated with T3, facing outwards. The thermocouple has served the SignalExpress software to record a phase change material temperature, which for simplicity, being the closest to the heat source, will indicate the maximum temperature reached by the PCM.

The next step is to introduce the water container into the passage created by the phase change material.



Figure 61 Container of water into the container of the PCM

Subsequent the phase change material container was covered with a simple plastic film, in order to avoid thermal dispersions.

After that a further thermocouple, indicated by T4, has been introduced into the phase change material, which will mainly serve to record an average temperature of the transient phase of the heat transmission in the material.



Figure 62 Containers covered by plastic film and Thermocouple T4 applied

Soon after, sawdust was introduced between the PCM container and the larger container.



Figure 63 Whole system covered by sawdust

The sawdust covers all smaller containers in such a way as to reduce the heat loss to the outside. Subsequently the whole system was closed by a cover of the same material of the larger container.

The same assembly procedure was carried out with butter. 1100 g of butter were applied inside the container and the thermocouples were inserted in the same established order.



Figure 64 Butter applied inside the container

After the butter, the material used for the heat exchange phase is paraffin wax. For this analysis 771 g of paraffin was used, applying it with the same procedure as the previous materials examined and with the same positioning of the thermocouples inside the system.



Figure 65 Paraffin wax applied inside the container

The last phase change material used to study a possible simulation of a thermal storage system is animal fat. Also for this assembly phase, the same procedure was applied and introducing the material with the weight of 1040 g into the container.



Figure 66 Animal fat applied inside the container

The final phase of the tests carried out is that of making the same temperature recordings over time without any phase change material. This test was carried out in order to have a comparison, at the level of temperatures, between the examined organic materials and the air.

4.2.3 SIMULATION THROUGH COMSOL MULTIPHYSICS SOFTWARE

The software COMSOL Multiphysics 4.3a has allowed to simulate the charging phase of the thermal storage system. The first phase is that of the construction of the system, which consists first of all in the choice of the component type, which has fallen into a 2D axisymmetric system. Subsequently, the size of the thermal storage system was introduced in such a way as to be able to reproduce the figure.


Figure 67 Introduction of the geometry of the system

The figure obtained with the applied dimensions is shown in the following illustration.



The next phase consists in attributing, for each domain, its representative material. Having the same materials as the previous simulation, we used the same data for each domain.



From the figure 70, it is clear that the material that differentiates the previous simulation is the PET which has been inserted on the contour of the water container in such a way as to simulate the presence of a separating layer between the PCM and the resistance tape.



The phase following the determination of the materials for each single domain is that of the application of the boundary conditions.

First of all, the choice of heat transmission in solids was chosen as the type of physics.

After that, the adiabatic condition for the edge and axial symmetry on the axis of the reference system have been attributed.

Subsequently, the initial temperatures for each individual domain were determined, thus applying a temperature of 293.15 K for the solid domains and a temperature of 333.15 K for the water.

The boundary condition that differs from the previous simulation is the application of a heat source on the edge of the water container.



Figure 71 Heat source applied into the boundary conditions

During the experimental phase, an attempt was made to give the resistance band a certain power so as to maintain a temperature of equal 75 °C recorded by the thermocouple connected to the temperature regulator.

To keep this temperature constant, the tape delivers 3% of the 500 W of power; moreover, not all the resistance tape is exploited but only 57.6% of its total extension.

Then:



$500 W \cdot 0.03 \cdot 0.576 = 8.64 W$

Figure 72 Heat source positioned on the edge of the water container

As can easily be deduced from the figure, only the side surface of the smaller cylinder is subjected to thermal stresses of the resistance tape.

Then the lateral surface of the cylinder is equal to 0.0259 m^2 , so the surface power generated will be 333.3 $\frac{W}{m^2}$.

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As for the mesh, also in this case we have set up a dense dimension of the elements, in order to have homogeneous and faithful results to reality.



Figure 74 Mesh applied on the thermal system

The final step that determines the simulation process of our thermal storage system is the determination of the study.



Figure 75 Transient study settings

Also in this case it was decided to make use of a transitional study with a simulation duration of 180000 seconds and with a time interval equal to 600 seconds.

At each time interval the temperature trend and the gradual variation of the temperature within the control volume were recorded.

5. RESULTS

The phase following the laboratory experimentation and simulation through the COMSOL Multiphysics 4.3a software is the discussion of the results obtained. In fact, through this phase it will be possible to describe the temperature trends that the materials take.

Through this discussion it will be possible to check whether the materials examined will indeed be excellent substitutes for the generic phase change materials used for the thermal storage process.

Moreover, based on the temperatures that we will obtain, it will be possible to determine a comparative analysis between the data obtained from the experimentation and the temperatures reproduced by the simulation in the software.

This last analysis will allow to determine how much the experimentation deviates from the data obtained from the simulation.

5.1 SMALL THERMAL STORAGE SYSTEM

As regards the first phase change thermal storage system data analysis process, 12 tests were carried out for each material.

These 12 tests served to determine that the melting of the material and the temperatures applied in the PCM almost always reach the same temperatures.

After that, a unique temperature pattern was chosen which allows to describe in the best of ways the temperature variation within the material taken into consideration. Subsequently this temperature trend was compared with the temperature trend obtained from the simulation in the software.

5.1.1 LARD

Regarding lard the choice of the test fell on the sixth, where it lasts 4399 seconds. The simulation, however, as for all materials has a duration of 5400 seconds with a time step of 100 seconds.

Then the next phase, the comparative one, we chose to analyze both analyzes up to 4300 seconds with a 100 second time step.

As can be seen from the figure 68, the temperature T4 is considered as the maximum temperature that can be reached by the lard during the heat exchange phase. The thermocouple is positioned beneath the cone-shaped container and, having little mass to melt, easily reaches high temperatures.

On the other hand, the average temperature T1 is the thermocouple placed under the PCM container, maintaining a trend that is almost low and very close to the temperature recorded in the insulation, T0.



Figure 76 Temperature trend obtained from test in the laboratory

What can be seen from the T4 temperature is that it not only easily reaches high temperatures, but returns to low temperatures over a much longer period.

This prolongation of the solidification phase would delay the cooling of the water (T2) and keep its temperature at 22 °C, therefore at a higher temperature than the ambient temperature.

A test was carried out, always on the same thermodynamic system and on the same phase change material but by applying a film on the exposed part towards the outside.

This choice is due to the simple fact of being able to contain the thermodynamic losses, of a convective nature, between the system and the external environment, so that the study can focus exclusively among the materials belonging to the thermal storage system.

In this case, for this type of analysis, four tests were carried out and finally the choice fell on the analysis of a single heat exchange test.

In this case, the second test realized it was useful for the discussion.

The first thing to highlight for this test is its duration. In this case the test of the thermal exchange between the materials has a longer duration, equal to 9439 seconds. It is also possible to notice that all the recorded temperatures, apart from the insulation one, assume higher values.



Figure 77 Secondo test made on the lard

This is verified by the increase in temperature recorded by the T3 thermocouple, positioned below the PCM container. This temperature increase describes that the heat exchange is concentrated between the materials belonging to the system and how the thermal exchange between the components and the external environment is practically nil.

Moreover, at the end of the test all thermocouples, except that attributed to the insulator, register more or less the same temperature.

What differentiates from the previous test is precisely the achievement of higher temperatures at the end of the test. These high temperatures mean that the PCM would be able to slow down the cooling of the water.

The next step is to simulate the reproduction of heat exchange and thermal storage using the COMSOL Multiphysics 4.3a software.

In this case, not only the temperatures suitable for a comparison with the laboratory test were determined, but the 3D images of the reproduction of the PCM container were extrapolated.

These 3D images describe the variation of the temperature over time to which the component under test is subjected.

In this case, the images that best describe the temperature variation have been chosen.



Figure 78 Temperature trend obtained from COMSOL simulation

What we can deduce from the figure is that the temperatures obtained from the simulation take on a trend almost similar to those obtained from the tests in the laboratory.

What differentiates the test from the simulation is how at the end of the simulation, the curves have difficulty re-joining and that the temperature trend of the water gets, at the end of the simulation, temperatures very similar to that of the maximum PCM temperature.





As can be seen from the history of the figures, immediately after 2000 seconds the PCM reaches a thermodynamic stability, the temperature scale varies much slower and the colour remains constant.

An interesting thing to note is the initial step. It has a constant colour on all the volume of interest, while the surface exposed to the water container has a different colour depending on the influence of the higher temperature. So what can be concluded is that the initial step is influenced by the boundary conditions imposed on the software. While the following steps mainly depend on the heat exchange between the hot and the environmental temperature domains.

The last analysis carried out from which we have extrapolated interesting results is a comparative analysis between the temperatures recorded by the laboratory test and those obtained from the simulation in COMSOL Multiphysics 4.3a.



Figure 79 Mean and Maximum temperatures obtained from laboratory and simulation

As can be seen from the figure, the T4 temperature recorded in the laboratory test reaches a lower maximum than that obtained from the simulation.

Furthermore, due to the thermal losses occurring between the phase change material and the external environment, the T4 cools much more quickly and reaches the thermal stability temperature much more quickly.

The trend of the average temperature, however, obtained by recording the laboratory data, is greater than that derived from the simulation.

What can easily be deduced is that with both the simulation obtained from the software and the data recorded by the laboratory test, the curves tend to reach an equilibrium temperature.

In the laboratory test the curves tend towards the temperature of 21-22 °C while from the simulation, the temperature trends tend to reach an equilibrium at the temperature of 30 °C.

Furthermore, based on the average and maximum temperatures of the two types of tests, a percentage deviation was made, used to visualize how much the laboratory test differs from the simulation reproduced by the software.

What is clear from the figure 80, is that the temperatures recorded by the laboratory test have lower values than those obtained from the simulation.

As far as the trend of the average temperature is concerned, a low percentage deviation is obtained only and exclusively at the beginning of the test, when both initial temperatures coincide.

While with regard to the maximum temperature, a reduction of the percentage deviation is obtained in correspondence of 300 seconds, when both trends reach the maximum peak of the temperatures.



Figure 80 Percentage deviation obtained between temperature trends

In fact, near the peak of temperatures, both trends, both the one obtained from the simulation and the one recorded by the laboratory test, record more or less the same temperature.

While towards the end of the tests, the percentage deviation, both relative to the maximum temperatures and that relating to the average temperatures, reach more or less the same value. These trends obtained towards the end of the tests and simulations are due to the simple fact that all the temperatures obtained from the tests tend to maintain the same value.

5.1.2 BUTTER

The second material examined for laboratory testing and simulation using the COMSOL Multiphysics 4.3a software is butter.

For this phase change material, during the laboratory test, 12 temperature recordings were made during the exchange and heat storage process.

As for the lard, and as for the other materials, this laboratory test is mainly used to verify if the material, if in contact with a hot source, easily reaches the melting temperature.

Among the 12 tests carried out on butter, the second test was chosen, which takes on interesting temperatures that are worthy to be described.

The duration of the second test in the laboratory is equal to 5188 seconds, so for the subsequent comparative analysis between the software simulation and the laboratory test, we will base ourselves on a duration of 5100 seconds.



Figure 81 Temperature trend of butter obtained during test in the laboratory

As shown in the figure, both the temperature trend T4, which would represent the maximum temperature reached by the PCM, and both the T1, which indicates the average temperature of the butter, reach high values in the initial phase of the test.

What is clear is that the temperature T2, which indicates the trend of water temperature, is cooled very quickly but then towards the end of the test, due to the modest temperatures of the butter, slows down its cooling phase maintaining constant its temperature and keeping with higher values with respect to the ambient temperature

Moreover, observing the figure, it is evident how the temperatures T1 and T4 assume a fundamental value during the cooling phase of the water and, above all the maximum temperature, takes on higher values with respect to T2 during the thermal discharge phase of the material.

This could be due to the thermal inertia properties of the phase change material taken into consideration during the data recording phase.

To reduce the thermal convective losses between the material and the external environment, a further test was carried out covering the whole system with a film in such a way that the heat exchange is concentrated only along the entire thermal storage system.

Also in this case, the tests carried out were four, but finally the analysis focused on the second registration test carried out.



Figure 82 Temperature trend with application of film on the system

What is possible to notice, is how in this case the inertial properties of the material have vanished but, on the other hand, the temperature trend T4 reaches much higher values.

Moreover, the effect of the heat exchange between the components of the system is increased, thus reducing the convective heat exchange between the material and the environment, is mainly due to the fact that the average temperature, T1, and the temperature T3 assume the same value.

Moreover, it is possible to notice how the temperatures reach more or less the same final value of the previous test, that in absence of film, but with a much longer test duration than the previous one. It is possible to notice that at the 5188th second of the test, all temperatures have higher values. This means that good thermal insulation with the external environment would reduce the thermodynamic losses and increase the thermal storage properties of the material and make the heat exchange phase longer.

With regard to the simulation carried out using the COMSOL Multiphysics 4.3a software, the temperature variation has been extrapolated throughout the phase change material.

The temperature trend in the PCM is not only determined by the analysis of the temperatures reproduced, but also by means of a simulation of the medium in 3D.

As in the previous simulation, the figures corresponding to certain phases of the material's fusion have been extracted.





From the first figure extrapolated from the software simulation, at time 0, it is highlighted how the body is influenced by the boundary conditions set.

The initial conditions that determine this phenomenon are: type of heat exchange and the high temperature of the hot water container that is in contact with the PCM.

From the hundredth second, on the other hand, the body tends to take on the coloration that mainly comes from the process of conductive heat exchange and from the process of thermal accumulation that assumes the material taken into consideration.

For the following steps, it is possible to notice how the increase in temperature in the medium progresses over time until a certain stability is achieved, highlighted by the slowing down of the variation in the colour scale.

In fact, just in the last figures, it shows how the maximum and minimum temperature reproduced by the legend, remain more or less unchanged.

The simulation carried out has a duration equal to 5400 seconds with a time step of 100 seconds. And then the following temperature trend has been obtained.

From the figure 83, it is highlighted how the recorded average temperature assumes an interesting temperature near the peak of the curve. Instead, the maximum temperature is recorded as it increases rapidly until a temperature peak of 312 K. is reached. What can be seen

from the maximum temperature is how it reaches the temperature values recorded in the water in the final phase of the simulation.



Figure 83 Temperature trend obtained from the simulation

As regards the temperature trend attributed to insulation, it maintains a constant value throughout the heat exchange process. Furthermore, unlike the laboratory test, the temperatures at the end of the simulation do not reach the same temperature.

This is possible due to the simple fact that the heat exchange carried out in the laboratory is more influenced by the convection between the system and the external environment.

A comparative analysis of the maximum and average temperature obtained through laboratory tests and software simulation was performed.

It is possible to notice, from the figure 84, how the maximum temperatures reach the peak very quickly, obtaining more or less the same result.

While the average temperature obtained from the simulation results to have higher temperature values than those recorded by the laboratory test.

Moreover, in the final stages, the temperature trends obtained by the software tend to converge towards a higher temperature than the temperatures recorded in the laboratory, but never reaching the same temperature at the end of the simulation.



Figure 84 Comparative analysis between temperature trends

Instead the curves describing the test in the laboratory, at the end of the test reach the same temperature. The maximum temperature, T4, of the laboratory test tends to lower much more quickly than the ideal trend obtained by the simulation. This behaviour is mainly due to the simple fact that the system reproduced by the laboratory is influenced by the convective heat exchange between the PCM and the external environment.

The final analysis performed on butter is to verify the percentage deviation between temperature trends. The extracted test is on the maximum and average temperature between the temperature trend obtained from the laboratory test and the simulation reproduced in the COMSOL Multiphysics software 4.3a.

This analysis was mainly addressed to determine how much the recording made by the laboratory test approaches with the values to the simulation reproduced through the software.

The fundamental thing that can be highlighted in the graph 85, is how both curves take more or less the same trend.

The interesting thing that is observed is that both the curves between the beginning and the 200 seconds both trends have a zero offset.



Figure 85 Percentage deviation obtained from comparative analysis

This cancellation of the deviation can be verified from the previous graph, where the curves obtained from the laboratory tests assume the same values of the temperature trends obtained by the simulation.

Subsequently, due to the sudden lowering of the temperatures of the temperatures T4 and T1, due mainly to the thermodynamic losses between the system and the external environment, they make the percentage deviations negative.

Towards the end of the tests, the deviations tend to have a constant value mainly due to the fact that the curves tend to maintain a temperature difference almost unchanged.

5.1.3 PARAFFIN WAX

As already mentioned above, paraffin is the most used material among those with phase changes for thermal storage systems. The material in question was analyzed in such a way as to have a large comparative study between organic materials and a phase change material generally used for thermal storage such as paraffin.

The laboratory test has a duration of 7396 seconds because the paraffin has a latent melt density and heat, equal to $230 \frac{kJ}{kg}$, thus making the phase change process longer than the other tests carried out on the others materials.

As for the other materials, 12 tests were carried out for the paraffin, making the choice on the first test carried out.

The figure 86, shows that the maximum temperature, T4, reaches the peak much more late than the other materials examined. This behaviour is mainly due to the property of thermal inertia that characterizes the material. This property determines the slow cooling of the paraffin until reaching, at the end of the recording, a higher temperature than the other temperatures recorded during the test.



Figure 86 Temperature trend obtained from tests in the laboratory

The temperature trend T2, which registers the cooling of the water, is lowered much faster, but maintaining, at the end of the test, a higher temperature than the ambient temperature.

On the other hand, the other recorded temperatures maintain a lower profile due not only to the thermal properties of the material, which makes heat conduction difficult, but also by the thermal dispersions between the thermal system and the environment.

In fact, by adding the film on the thermodynamic system, to reduce the heat loss, slight improvements are noted.

Initially four tests were carried out with this further modification, making the choice for the analysis on the second registration fall.



Figure 87 Temperature trend with application of a film layer on the system

What is more easily deduced from the figure 87, is that the temperature profiles attributed to the material take on higher values. These values are mainly due to the fact that the conductive thermal exchange within the material prevails over the convective heat exchange between the system and the external environment.

Moreover, this last phenomenon that is evident from the temperatures can be noted also by the duration of the test itself.

In fact, the duration of the test is much higher than the previous one. This is due to the fact that the reduction of thermal losses with the outside has allowed the cooling of the material and water to slow down.

Furthermore, it should be noted that, at the end of the test, the temperatures reach and remain at higher values with respect to the heat exchange process without the film.

The next phase consists in the analysis of the data obtained from the simulation carried out using the COMSOL Multiphysics 4.3a software.

The heat exchange process was performed for a test lasting 5400 seconds with a time interval of 100 seconds.

Of course, what will be seen as the short duration of the simulation, compared to the laboratory one, does not at best describe the process of heat exchange. So it will be interesting to see how the thermal profiles obtained from the software differentiate from those obtained from the laboratory test.



Figure 88 Temperature profile obtained from software simulation

As already mentioned, it is possible to note from the figure that the thermal profiles obtained do not reach their thermal stability characterized by the achievement of a single temperature value at the end of the simulation.

In fact, the maximum temperature, at the end of the test, assumes a value very different from other temperatures. On the other hand, the maximum temperature reaches a peak much more quickly, but with a very similar value, compared to the laboratory test.

On the contrary, the average and minimum temperature take on much higher values, precisely because the boundary conditions attributed to the system make the whole control volume much more isolated and with heat exchanges with the outside environment that are not very relevant. Subsequently, an analysis of the temperature variation on the phase change material was carried out using the figure reproduced by the COMSOL software simulation.





From the first figure, at step zero, it is possible to notice how the colour of the body is clearly influenced by the boundary conditions making the part of the material in contact with the hot water container of a different colour from the rest of the body. Subsequently the evolution of

the process is mainly influenced by the conductive heat exchange inside the material. In fact, between one step and another, one notices how the colour progresses, thus highlighting the gradual increase in temperature within the body over time.

In the final steps a thermal stability is achieved, evidenced by the slowing down of the variation in colour of the volume taken into consideration. In fact, from the last steps of the simulation it is possible to notice, through the temperature legend, how the temperatures in each part of the body remain unchanged.

The final phase of the paraffin study consists in the comparative analysis of the average and maximum temperatures obtained from the recording of the laboratory test and the simulation of the COMSOL Multiphysics software 4.3a.

First of all, having different durations, it was necessary to shorten the duration of the laboratory test up to 5400 seconds of the simulation, in order to analyze the thermal profiles over the same time duration.

Furthermore, not only were the temperature trends of the two types of tests analyzed, but also the percentage deviation. This further analysis was carried out in such a way as to be able to visualize how much the temperatures recorded in the laboratory approximate the values, almost ideal, obtained from the simulation.



Figure 89 Comparative analysis of temperature obtained from test in the laboratory and software simulation

A very interesting thing that emerges from the figure is how the maximum temperature T4, obtained from the recording of laboratory data, takes on greater values than the simulation. However, always the maximum temperature T4, is cooled much faster than the maximum temperature obtained from the simulation.

In fact, towards the 5400th second one shows how the simulation temperature trend takes on higher values, ending the test with a higher temperature.

This means that in the laboratory, the maximum temperature liquefies much faster but, because of the heat loss between the system and the external environment, it cools much more quickly. As for the average temperatures, the temperature trend obtained from the simulation assumes higher values for the whole duration of the test. Finally, due to the lack of thermal dispersion between the system reproduced for the simulation and the external environment, at the end of the tests the thermal profiles obtained from the laboratory test reach lower values than those obtained from the simulation.

The final phase of the comparative analysis, between the thermal profiles obtained from the laboratory test and those obtained from the simulation, consists in reproducing the percentage deviation.

In fact, the main purpose is to be able to visualize how much the thermal profiles recorded by the laboratory test differ from those obtained by simulation through the COMSOL Multiphysics 4.3a software.



Figure 90 Percentage deviation of comparative analysis

What has already been described above is easily apparent from the figure. As far as the maximum temperatures are concerned, an initial negative percentage deviation is deduced and then canceled.

This behaviour is due to the fact that the thermal profiles of the laboratory decrease much faster than those of the simulation. The thermal profile of the maximum temperature obtained from the simulation assumes, before 0%, lower values than the maximum temperature profile obtained from the laboratory test. Immediately after 0%, the thermal profile of the simulation records higher values than the temperatures obtained in the laboratory.

This same behaviour is clearly visible also for the percentage deviation attributed to average temperatures. In this case, however, the zero value is obtained at the beginning of the tests while for the rest of the analysis, the percentage deviation assumes a negative and constant value.

5.1.4 FAT

The last material taken into consideration for the study for a possible thermal storage system with phase change material is the grease obtained from the post-firing phase.

For this last case study, the analysis focused on an evaluation of the data obtained from a laboratory test and a simulation reproduced using the COMSOL Multiphysics software 4.3a. Subsequently, certain temperature trends were taken from both types of tests and a comparative analysis was performed.

As for the previous phase change materials examined, 12 tests were carried out and the analysis ultimately fell on the last recording of the data.

The laboratory test found a remarkable duration of 15053 seconds, which allowed to analyze in detail all the temperature evolutions during the exchange and thermal storage phase.

Subsequently, as regards the comparative analysis, in order to have a good comparison between the two tests, a study was carried out for the duration of 5400 seconds, which would correspond to the entire duration of the simulation performed through the software.

From the figure 91, it is possible to notice how the temperatures close to the fat, take more or less the same values. This means that the material heats up very quickly, even reaching values close to that of melting.

Furthermore, it is clear that the temperatures of the PCM are kept higher even in the following phases with respect to the temperatures recorded by the T2 thermocouple, which records the temperature trend of the water.

From these trends, it is explained the high duration of the test compared to the other recordings made on the other materials.



Figure 91 Temperature profile calculated by test in the laboratory

In fact, the fat tends to cool much more slowly, thus having a much longer discharge and solidification phase.

This slowing down of the phase change material cooling, allows to slow down the cooling of the water and making it reach, at the end of the test, a temperature slightly higher than the ambient temperature.

For a possible verification on the material a film has been placed on the entire system in such a way as to be able to concentrate the heat exchange between the various layers of the system and minimize the convective thermal transmission between the system and the external environment.

For this phase of the tests, four data records were made and at the end the choice fell on the last laboratory test.

The first thing that emerges from the figure 92, is that as regards the duration of the recording remains more or less unchanged, maintaining a consistent length of the test.

The temperatures attributed to the phase change material, on the other hand, reach high values much more quickly.



Figure 92 Temperature trend of the system with film

While in the following seconds, those affected by cooling, the values are kept much higher. This slowing down of the cooling phase of the grease thus entails a possible slowing down of the water cooling.

Finally it is clear how the temperatures attributed to the material and that of the water, in the final phase of the test, maintain high values. Therefore, these higher temperatures describe that the thermodynamic losses with the external environment have been reduced and that would thus make the entire system, a possible thermal storage component with phase change material.

To perform a possible verification of the values recorded by the laboratory tests, the system was also reproduced on the COMSOL Multiphysics 4.3a software.

The duration of the test, in this case, is equal to 5400 seconds with a time interval of 100 seconds. For each time step, both the temperature recordings and the chromatic variation of the material over time were made.

The figure 93 shows that the temperature trends attributed to the phase change material reach temperatures almost very similar to those recorded by the laboratory test.

What differentiates is the duration that is much shorter than the previous test. But this duration mainly reflects the lack of achievement of the same value, by the temperature trends, at the end of the test.



Figure 93 Temperature trend obtained from simulation

It should be noted that the average water temperature trend and the maximum PCM temperature reach the same values at the end of the simulation, while the other curves remain at lower values. Furthermore, having a shorter duration, the temperatures recorded at the end of the simulation take on very high values. These last data allow to analyze the ideality of the whole system, reproduced by the software, characterized by thermodynamic losses with the external environment practically nil.

Subsequently, in order to verify the evolution of the thermal conduction within the phase change material, an analysis was also carried out on the figure reproduced by the software.

The significant phases of the simulation have been chosen as it would allow to better describe how the temperature inside the body examined varies.





The initial step presents a coloration, on the whole body, very different from the other figures represented by the following steps. This differentiation depends mainly on the fact that the initial phase depends mainly on the boundary conditions.

In the subsequent phases it is clear how the material being examined is influenced by the conductive heat exchange inside the medium.

In fact, it is possible to notice the progress of the red colour, to which the highest temperatures belong, within the PCM.

While in the final stages of the simulation the coloration and temperatures described by the legend do not increase. This slowing down of evolution shows how the body, towards the end of the simulation, reaches its thermodynamic stability and therefore the conductive thermal exchange tends to slow down.

The final phase of the analysis performed on the fat is that of a comparison of the temperatures between the data recorded by the laboratory test and the temperatures obtained from the simulation of the COMSOL Multiphysics software 4.3a.

As already mentioned above, the analysis was carried out on the basis of the duration of the software simulation in order to have a comparison on the same time period.

The average and maximum temperatures of the two tests were taken into account.



Figure 94 Comparative analysis between test in the laboratory and the simulation

A very interesting thing found in the figure, is how the temperature trends are very similar until recording, for most of the study period, the same temperature values.

As for the maximum temperature, both curves assume the same tendency except in the final phase of the test. This is mainly due to the simulation's ideality, as the temperature obtained from the software is higher than the data recorded by the laboratory test. This ideality of the simulation allowed to determine how the thermodynamic losses between the system and the external environment are less than the laboratory test. In the laboratory test, however, the phase change material, being more conditioned by the external environment, cools much more quickly in the final stages of the test.

While for curves describing average temperatures, it is possible to notice that both curves assume the same values for almost the entire duration of the test.

Finally, it is noted at the end of the test how the curves referring to the laboratory test are reunited unlike the temperatures obtained from the simulation.

In fact, as already noted above, the duration of the simulation is greater than the test in the laboratory, precisely because the system reproduced by the software is not heavily influenced by the surrounding environment and therefore the temperatures, especially the maximum, are maintained higher obtaining a re-joining of the two curves over a period of time greater than 5400 seconds.

To check how much the data recorded by the laboratory test deviate from the simulation, an analysis was carried out. This analysis consists in verifying the percentage deviation of the curves.



Figure 95 Percentage deviation between temperature profiles obtained from test in the laboratory and simulation

The curves of the percentage deviations confirm what is visible from the previous figure. In fact the percentage deviation curve referred to the average temperatures is a constant close to 0% precisely because for the entire duration of the test the average temperature curves, both the one obtained from the laboratory test and the simulation one, are roughly same temperature values.

Also the percentage deviation curve referred to the maximum temperature, assumes a percentile deviation which is very low.

In the initial phase of the test, both percentage deviations have high values. This is mainly due to the fact that the simulation is started with fixed temperatures inserted in the settings, while the laboratory test starts from very different temperatures influenced by previous tests.

5.2 SCALE REPRODUCTION

The scale system reproduced in the laboratory made it possible to simulate a thermal storage system that could be introduced into a solar thermal system to replace the typical thermal storage system.

In this case, the tests carried out have had a considerable duration. This is due to the slow release of thermal energy to the outside, and as we tried to reproduce both the charge and discharge phase, data were recorded for the entire duration of the test.

Subsequently, a reconstruction was carried out using the COMSOL Multiphysics 4.3a software and we tried to reproduce the single charge phase of the single material in question.

Finally, both phases of the two tests were taken and a comparative analysis of the two tests and a subsequent percentage deviation of the recorded temperature trends was carried out.

5.2.1 LARD

The lard is the first material taken into consideration for this second type of tests carried out in the laboratory. For this PCM two registrations were made and at the end the choice fell on the second test.

The entire charge and discharge phase lasted for 190833 seconds, which allowed us to verify the thermal storage properties of the lard. Subsequently, the simulation was carried out using the software in such a way as to record the behaviour of the material in the charge phase only. This test reproduced on COMSOL Multiphysics 4.3a, as well as for the other simulations made for the other materials, has a duration of 18000 seconds in order to observe the charge phase of the material.

Finally, a comparative analysis was carried out between the two tests, in the laboratory and by the software, and a percentage deviation of the two tests, so as to check how far the temperatures recorded by the laboratory test deviate from the data obtained from the simulation of the software.



Figure 96 Temperature trend obtained from the second test

As can be seen from the figure 88, the maximum and average temperatures reach very high valour very quickly, while the minimum temperature reaches values similar to other trends with much delay. Moreover, the maximum temperature reaches, at the beginning, it gets a peak and then falls to a stable value. This peak is probably due to the influence of the resistance being, the thermocouple T3, very close.

After all three curves, relative to the phase change material, reach more or less the same value, the resistance is switched off and the PCM discharge process starts.

During this phase the material cools very slowly, recording, at the end of the test, the temperatures higher than the ambient temperature.

As for the temperature related to water, not having a thermocouple that records its temperature variation, it is possible to determine the temperature obtained in the final phase of the test. The value is determined by restarting the temperature regulator, which registers a value of 23 ° C. This means that the phase change material delays the cooling of the water and keeps it, at the end of the recording, at higher values than the temperature of the external environment.

Subsequently, a simulation of the material charge phase was carried out using the COMSOL Multiphysics 4.3a software. The duration of the simulation is equal to 18000 seconds, and will remain the same for the other materials examined. For the data acquisition, a time interval of 600 seconds has been set.



Figure 97 Temperature profile obtained from the simulation

What emerges from the figure in question is how the heat source affects the material a lot. In fact, at the end of the test the material continues to heat up and to reach higher and higher values. Furthermore, unlike the laboratory test, the minimum temperature trend increases very slowly.

This means that the material heats up much more slowly in the contour of the PCM container.

The maximum temperature heats up very quickly in the initial stages of the test, but without reaching its stability in the phases following the peak.

Through the software COMSOL Multiphysics 4.3a, it was possible to check the temperature trend by displaying the material in question reproduced in 3D.







Tempo=7200 s Volume: Temperatura (K)








In the first figure shown, it is evident that the inner part of the cylinder has a very different colour than the rest of the body. This is mainly due to the boundary conditions set initially in the software.

What emerges from the figures is how the body temperature increases rapidly from the first moments of the test.

Instead, towards the end of the test, it shows how the temperature continues to increase, even if with a shorter speed than the initial part of the simulation. This is due to the fact that, in the seconds near the end of the simulation, the temperature is very close to achieving its thermodynamic stability. This stability, which characterizes the material, constitutes the phase of transposition of one phase to another.

All these differences, between the laboratory test and the simulation carried out by the software, are highlighted by the subsequent figure in which a comparative analysis was presented between the two tests.



Figure 98 Comparative analysis between the two tests

In this case, the laboratory test reaches high temperatures for a shorter period than the one set for simulation. In fact, the charge phase recorded in the laboratory has a duration of 11283 seconds, and therefore the comparative analysis was made over a duration of 10800 seconds. What emerges from the figure, is like the maximum temperature of the test in the laboratory, reaches the maximum peak much more late than that obtained from the simulation.

Furthermore, the maximum peak of the laboratory test has higher values than the simulation. Towards the end of the test, due to the continuous heating of the material, higher values are recorded during simulation than those obtained from the laboratory test.

On the contrary, the average temperature recorded during the laboratory test maintains higher values than those obtained from the simulation, for the entire duration of the analysis.

Also the trend of minimum temperature assumes the same behaviour, but only towards the end of the whole duration.

While temperature trends attributed to the insulation maintain the same values for the duration in question.

Finally, to verify the veracity of the test in the laboratory compared to the simulation, a percentage deviation was made between the temperature trends.



Figure 99 Percentage deviation obtained from temperature profiles of the two tests

The most interesting curve to be taken into consideration is that of maximum temperatures. In which it is clear how the curve reaches 0% in two different periods. This is due to the fact that

the two curves obtained from the different tests intersect, and register the same values, in two different phases of the test.

The cancellation of the percentage deviation is obtained, even for a long period, even for the minimum temperatures. As they tend to have the same temperature value for a consistent period. The percentage deviation relative to the temperature trends of the insulation, on the other hand, tends to have a null value for the entire duration of the test.

The percentage deviation relative to the average temperatures never reaches zero values, due to the simple fact that the two curves never cross each other and that the temperature trend recorded in the laboratory maintains higher values than those obtained by the simulation, for the entire duration of the test.

5.2.2 BUTTER

The second material taken in exam for the scale test carried out in the laboratory is butter. This test also has a considerable duration, mainly due to the slow cooling of the material and the difficulty in releasing heat to the external environment.

In fact, the actual duration of the entire test is about 177871 seconds, in which a good percentage of the duration belongs to the phase of the component discharge.

For this type of material, two tests were carried out in the laboratory to then choose the first one to display the temperature trends.



Figure 100 Temperature profiles obtained from the first test made in the laboratory

The first thing you notice from the figure 100, is the oscillatory behaviour that the temperature trends take. This is due to the difficulty of the thermocouples in recording the temperatures of the material at best. In fact, the butter is largely composed of water, which has very different properties from the remaining part of the component. This differentiation made data logging more difficult.

After that, it is clear how all the three curves attributed to the material have roughly the same trend. In addition, all three curves, I reach the peak very quickly, so I allow, for the remaining part of the test, the cooling of the body.

In this case, it was not possible to record a water temperature history. However, it was possible to determine the final temperature by reigniting, at the end of the test, the temperature controller that is connected to both the electrical resistance and a thermocouple sound.

In this case, the temperature reached at the end of the test is 24 °C, therefore slightly higher than that obtained by the lard.

This allows us to conclude that even if there have been some difficulties in the data recording phase, the butter has excellent performances in the thermal storage phase.

This feature allowed us to check how the water, at the end of the test, becomes warmer and no longer reaches temperatures equivalent to the environmental ones.

The phase following the laboratory test was that of simulation using the COMSOL Multiphysics 4.3a software.

This reproduction made it possible to verify, from the most realistic point of view, how the phase change material behaves in proximity to a heat source such as resistance and hot water.

Unlike the test in the laboratory, only the charge phase of the material was shown, which, also in this case, has a duration of 18000 seconds with a time interval, between one step and another, of 600 seconds.

As well as in the realistic phase reproduced in the laboratory, even in the simulation, reproduced in the figure 101, the temperatures reach the peak very quickly. In the subsequent phases of the simulation, there is no real thermodynamic stability but the material continues to increase with a lower slope than that of the initial phase.

All the curves, unlike that attributed to the insulator, have more or less the same behaviour, but with different values mainly due to the different positioning of the thermocouples inside the material simulated in the software.



Figure 101 Temperature trends obtained from the simulation

Moreover, the oscillatory behaviour seen from the data recorded by the test in the laboratory, in this case are not shown because we have introduced data, related to the butter, more ideal, thus maintaining the continuous curves.

The variation of the temperatures inside the phase change material was also verified by the variation of the body colour, during the simulation, reproduced in 3D by the software COMSOL Multiphysics 4.3a. The most significant steps have been chosen, so as to be able to see in detail what has already been observed by the temperature profiles obtained during the simulation.





What is highlighted in the figures is how, from the initial step and the next step, the difference in colour is substantial.

This difference is due, as previously stated, by the rapidity of the material to reach the temperature peak. In fact in the following steps, the colouring remains almost unchanged as the temperature continues to increase but much slower.

Instead, in the initial step, it is clear how the inner part of the cylinder has a very different colour than the rest of the body. This is essentially due to the initial conditions set in the software which shows that the inner part of the cylinder is sung with a warmer component and the heat source.

The next phase of the study consists of a comparative analysis between the data obtained in the laboratory and those of the simulation.

As already mentioned, only the two charge phases of the tests will be considered and as the one obtained from the laboratory has a shorter duration, the analysis has been adapted to the duration of the laboratory test. In fact, the comparative analysis is based on a duration of 7200 seconds.



Figure 102 Comparative analysis between the two studies

The figure shows how the two tests found very different results. As already mentioned above, this difference is due to the particularity of the material that has a good amount of water inside it so as to compromise the test.

While in the simulation we have attributed data to the material so as to make it as ideal as possible. In fact, the maximum temperature reached in the laboratory test is much lower than that found in the simulation.

However, the minimum and average temperatures of the laboratory test are very similar to each other and they already have values much closer to those obtained by software simulation. Finally, the temperatures attributed to the insulator have the same values during both tests. To verify how much the curves differ from each other, a percentage deviation has been made.



Figure 103 Percentage deviation obtained from profiles temperature of the two tests

The percentage deviation equal to the maximum temperatures is almost always different from 0% because they never reach the same value for the whole duration of the test.

In addition, the percentage deviations attributed to the average and minimum temperatures have an oscillating behaviour.

The percentage deviation of the minimum temperatures is canceled at two points on the curve, which means that during the tests the minimum temperatures reach the same value twice. The percentage deviation of the average temperatures is the same as that of the minimum temperatures but almost always has a negative percentage deviation throughout the duration of the test. Furthermore, during the test phase, both temperatures never reach the same value. Instead, the percentage deviation attributed to the temperatures recorded on the insulation has a constant trend close to 0%. This is due to the fact that for the entire duration of the test, the two temperature trends always take the same values.

5.2.3 PARAFFIN WAX

Paraffin wax is the most used material for thermal accumulations with phase change material. This test was made in such a way as to be able to verify how much organic waste materials are approaching the temperatures obtained during the laboratory test.

In fact, paraffin has excellent thermodynamic properties such as to allow it to be used for thermodynamic storage. Among these properties, it is worth noting the latent heat of fusion of the material that is higher than the other bodies taken into consideration. This allows having a high thermal inertia such as to delay the cooling of both the water and the paraffin itself.

The laboratory test lasted 189076 seconds, and therefore approximately equal to the tests carried out on the other materials, so as to be able to determine a comparative analysis between the paraffin and the organic waste materials on the same temporal duration.

Also, for the paraffin wax two tests of recording were made and then the choice was made for the discussion of the results on the first one.

As can be seen from the figure 104, the material in question reaches the peak much later than other materials. However, after shutdown the cooling of the phase change material maintains high temperatures for a certain period of time and therefore cooling is much slower.



Figure 104 Temperature profiles obtained from test in the laboratory

Furthermore, it is important to observe how in the initial vessels of the test, the thermocouple attributed to the average temperature has higher values than the maximum one. This is possible due to the different positioning of the thermocouples within the body in question and their possible movement during the melting of the material.

In the final stages of the test it is highlighted that all the profiles of the temperatures attributed to the material reach the same value.

Regarding the temperature trend related to heating and cooling of the water, it was not possible to record any value during the test.

On the other hand, by reigniting the temperature regulator for the test following this test, it is possible to view the final temperature of the discharge phase. In this case the final temperature attributed to the water is around 29 °C which means that the water keeps warm even if the phase change material, in the same phase of the test, maintains lower temperatures.

The next phase of the study is the simulation performed using the COMSOL Multiphysics 4.3a software.

For this step, only the phase load of the phase change material, which is expected to have a duration of 18000 seconds with a time interval of 600 seconds, was based only on the phase.



Figure 105 Temperature trend obtained from the simulation

Unlike the test done in the laboratory, reaching the temperature peak, referred to the maximum temperature, occurs much earlier. This is due to the ideal behaviour that the entire thermodynamic system assumes. Instead the average and minimum temperatures gradually increase.

Immediately after the peak, the temperature trend, referred to the maximum temperature, does not remain constant but continues to increase.

These temperature variations, shown in the previous figure, were then highlighted by the 3D reproduction of the body and how the values obtained vary over time.

We have examined only some stages of the test, such as to verify how the material behaves if placed in contact with a source of heat such as hot water and resistance.





The fundamental thing that emerges from the first figures is that between the first and second the coloration is very different. This is due to the fact that the material, in the early stages of the simulation, heats up very quickly.

While in the following steps, the colouring varies very slowly, as the material continues to heat up but with a lower speed than the initial seconds of the test.

In step zero, finally, it is possible to notice how the colour of the inner part of the cylinder is very different from the rest of the body examined. This is due to the initial conditions set on the software, because, despite having the initial temperature of 273.15 K, the inner part of the medium is in contact with a hot body and this affects its colour.

The final phase of the paraffin study is a comparative analysis between the data recorded in the laboratory test and those obtained from the simulation. For both tests, the charge phase was considered and in this case, as the data recorded in the laboratory lasted 41506 seconds, the comparative analysis was carried out on a single test lasting 18000 seconds.



Figure 106 Comparative analysis between temperature profiles obtained from the two tests

It is possible to notice that the maximum temperature obtained from the simulation recorded higher values than those obtained from the laboratory test.

Instead the other temperatures obtained assume more or less the same values throughout the entire duration of the test.

To conclude this comparative analysis, a study was carried out on the percentage deviation between the two tests.

This was used to verify how much, the data obtained in the laboratory, deviate from the temperatures obtained from a more ideal study such as simulation made using the software COMSOL Multiphysics 4.3a.



Figure 107 Percentage deviation calculated between the two tests

What you notice from the figure 107, has already been well discussed by comparative analysis of thermal profiles.

That is, the percentage deviation attributed to the maximum temperatures assumes, for the entire duration of the test, values well distant from 0%.

On the other hand, the other percentage deviations relative to the other temperature trends take on values close to zero for the entire duration of the test, as they maintain very similar values.

One of the materials used as a case study for thermal storage with phase change material is animal fat.

This fat has been obtained from a previous cooking phase of the meat itself and has served to understand if an organic waste material can easily be reused for a possible thermal storage phase.

In the next results that will be illustrated, it will be possible to see how this material takes on characteristics that can be taken into account.

The first part of the analysis coincides with a recording of the data by a laboratory test. This phase lasted for 195289 seconds and, having carried out two registration tests, the choice for the following discussion fell on the second.



Figure 108 Temperature trend obtained from the test in the laboratory

As can be seen from the figure 108, the maximum temperature trend reaches the peak with respect to the other temperatures attributed to the material taken into consideration. Immediately after that it reaches its thermal stability, in which the melting phase of the material corresponds, up to the beginning of the discharge phase of the material.

As for the other temperatures, during the charging phase, the minimum temperature trend reaches higher values than those recorded by the T4 thermocouple, for the average temperature. This particularity will be due to the positioning of the thermocouples but that, however, having acceptable values we have considered them for the analysis. Moreover in the following phases the average temperature returns to have higher values than the minimum.

As regards the discharge phase, the curves tend to have higher values than the ambient temperature. This determines that the fat cools much more slowly, keeping the water warmer and dispersing as little thermal energy as possible.

In fact, at the end of the test it is possible to check the final water temperature, which in this case corresponds to 26 °C. Therefore the final temperature of the water has a value far higher than that of the external environment and above all of the final temperatures recorded in the other materials previously examined.

For a more in-depth analysis, a simulation was performed using the COMSOL Multiphysics 4.3a software. For this part of the test, only the charge phase to which the material is subjected, with a duration of 18000 seconds and a time interval of 600 seconds, is considered.



Figure 109 Temperature profiles obtained from the simulation

From the simulation, it has been shown that the maximum temperature of the material rises very quickly and then, after reaching a peak, the maximum temperature increases much more slowly than the initial phases of the simulation.

The average and minimum temperature increase but gradually and without peaks within the curve. On the contrary, the temperature related to the insulation remains almost low and close to the ambient temperature.

To highlight how these temperatures vary within the material, the body was studied by observing 3D reproduction. Some significant phases of the simulation have been chosen to describe the temperature trend into the body.





The substantial difference that can be seen from the beginning is how from the first to the second step the colouring is totally different. This is due to the fact that the material heats up quickly already in the early stages of the simulation while in the subsequent phases the colouring progresses gradually.

The first step of the simulation shows how the colouring is highlighted by the boundary conditions inserted by the software settings.

In fact the inner part of the cylinder has a very different coloration with respect to the different parts of the body since the inner part of the material is in contact with a heat source.

The final phase was to determine a comparative analysis between the data recorded in the laboratory and those obtained from the simulation.

In this case, only the charging phases of both tests were taken into consideration and based on the duration of the simulation, of 18000 seconds, since the duration of the laboratory test is much longer than the simulation, therefore the comparative analysis is been made on a temporal phase.



Figure 110 Comparative analysis between results of test in the laboratory and the simulation

The figure shows how temperature trends take on more or less value, unlike the maximum temperatures recorded for both tests. In fact, the data obtained from the simulation maintain values far higher than those recorded in the laboratory test.

To verify how much the two tests differ from each other, a percentage deviation has been made.



Figure 111 Percentage deviation made at the end of the comparative analysis

What emerges from the figure is what has been noted in advance, namely that the maximum temperatures of the two tests, never assume the same value.

While the percentage deviation relative to the average temperature has a different value of 0% because in the initial phase of the tests, the two curves assume different values. Instead in the final phase, the two curves tend to re-join and therefore the percentage deviation tends to approach towards 0%.

The percentage deviation relative to the minimum temperatures is different from 0% but still maintains constant and low values, which means that the two curves obtained from the two tests tend to have temperatures very close to each other and with a constant temperature difference for the intact duration of the test.

Finally, the percentage deviation relative to the temperature of the insulation is almost constant and close to zero.

5.2.5 AIR

The last test performed in the scale component is the one without phase change material. This was mainly used to verify how the phase change technologies affect the thermal transmission phase.

Also in this case, the test was made with a duration approximately equal to the previous ones, so as to be able to verify the charge and discharge phase during the same time period. In this case the test lasted 191055 seconds and, unlike the materials, only one data recording test was performed.



Figure 112 temperature trend obtained from the test in the laboratory

What emerges from the figure is how all the temperature profiles attributed to the material increase immediately, in the vicinity of the instant 0. In the subsequent phases the temperature remains constant until the start of the discharge phase.

When the electrical resistance is switched off, the air is suddenly cooled until, at the final moment of the test, it returns to values close to the environmental values.

This means that the air, not accumulating any amount of heat, cools quickly. Indeed, even water returns to the initial test temperatures, which means that all the accumulated heat has been released during the entire discharge phase of the test.

The graph shows that the profiles attributed to the average and minimum temperatures have more or less the same values, probably due to the close positioning of the thermocouples.

As for the charging phase, the simulation was carried out using the COMSOL Multiphysics software 4.3a.

The simulation was carried out in order to verify how the body behaves, from the most ideal point of view, if in contact with a thermal source.

The duration of the simulation is 18000 seconds and with a time interval of 600.



Figure 113 Temperature trend obtained from the simulation

The simulation produces very different results from the laboratory test. In fact, it is clear how the profiles attributed to the average and minimum temperatures have very different values. Furthermore, the maximum temperature trend after the rapid reaching of high values does not maintain its stability but the temperature continues to increase.

The simulation carried out by the software allowed to check the temperature history by displaying the variation of the 3D volume colour reproduced by the software itself.

In this case, significant steps have been chosen, in order to be able to better comment on how the body behaves under the influence of a heat source.

From the follow figures, the main thing that you notice is how the first two steps identified, they differ from each other. This is due to the sudden increase in temperatures already from the initial instants of the test.

In the following phases, however, the temperature continues to increase but there is a much lower speed compared to the initial seconds of the simulation.





Moreover, it is possible to notice, in the initial step of the simulation, how the internal part of the cylinder has a very different colour to the remaining part of the body. This is due to the boundary conditions imposed in the software, as the inner part of the cylinder is in contact with a heat source.

A comparative analysis was performed to verify how much the two tests differ. This analysis was done only for the charging phase. As the test carried out in the laboratory has a longer duration, the comparison was based on the duration of the simulation, i.e. 18000 seconds.



Figure 114 Comparative analysis between the results of the two tests

What emerges from the figure is how the profile of the maximum temperatures have similar values only in the initial phase of the test while in the subsequent instants the temperature trend of the laboratory test remains constant while the data obtained from the simulation continues to increase.

On the other hand, the average temperature trend obtained from the simulation has more or less the same values as those obtained from the laboratory test. While the minimum temperatures have different values for the entire duration of the test.

To see in more detail how much the two tests differ, the percentage deviation for all the temperature profiles of the obtained temperatures has been calculated.



Figure 115 Percentage calculated from the comparative analysis

The percentage deviation relative to the minimum temperatures is the most interesting curve. In fact, it tends to have an almost constant trend throughout the study but with very high values. On the other hand, the percentage deviations of average temperatures and insulation temperature are those that tend to have a value close to 0%. While the percentage deviation relative to the maximum temperature has a percentage deviation close to 0% in the initial phases, as the two tests in these first moments tend to assume the same values, and then increase.

5.3 RESULTS OF THE DSC ANALYSIS

Through the DSC analysis it was possible to verify the amount of latent heat exploited during the temperatures recorded by the laboratory tests in the phase of charge and discharge of the phase change material.

Furthermore, a comparative analysis was made regarding both the recorded temperatures during the tests and the effective melting phase of each material.

Finally, for each PCM, the specific heat at constant pressure before and after the phase of the entire body fusion has been obtained through the previous equation.

5.3.1 LARD

The first material taken into consideration is lard, from which a sample of 13.2 mg was used. Through the DSC analysis it was possible to determine the specific power, expressed in W/g, when the temperature varies. For this phase of the analysis, we considered a temperature range that goes from -20 $^{\circ}$ C to 90 $^{\circ}$ C.

For the extremes of this temperature range there was a duration of 1 minute whereas for the internal values a temperature variation of 10 $^{\circ}$ C/min was used.

By varying the temperature, it was possible to visualize peaks that would correspond to the moment of the material's melting. This phase is visible through the sudden peaks represented by the following figure.



Figure 116 DSC results of the lard

From the figure 116, it is possible to see how, in the same examination, both the charging phase, indicated by the negated values of the specific power, and the discharge phase, indicated by the

positive values of the function, was carried out. It was possible to view displays, through the peaks of the function, where the melting and solidification phase of the material takes place. As for the charging phase, the peaks occurred at $6.0857 \degree C$ and ended at $51.88 \degree C$.

By means of the equation that expresses the function, it was possible to perform the subsurface area. This made it possible to calculate the latent melting heat of the lard which corresponds to a value of 121 kJ / kg.

However, the experimental phase examined in the laboratory has a temperature range from 20 $^{\circ}$ C to 52 $^{\circ}$ C, which means that not all the latent fusion heat, usable for the material, has been exploited. In fact the latent heat exploited in the practical phase corresponds to 88.4756 kJ / kg. In fact, at the 52 $^{\circ}$ C reached by the material, the complete melting of the material does not take place. These calculations were possible through the use of the Matlab R2015b software, which allowed, through the 'trapz' function, to be able to calculate the underlying area of the function. As for the discharge phase, not being involved in the study carried out in the laboratory, it was calculated the latent heat of solidification of the material in the temperature range from 52.0465 $^{\circ}$ C to 20.0408 $^{\circ}$ C, which is equal to 98.5260 kJ / kg.

From this last datum it is highlighted how for solidification, the material needs less energy than the melting phase.

Moreover, through data obtained from the DSC study, it was possible to obtain the specific heat at constant pressure before and after the melting phase of the medium.

Through the comparative calculation between the examined material and the sapphire, it was possible to obtain the specific heat at the extremes of the melting range of the organic material. In fact, it was found that in correspondence with the 6.0857 °C, in the solid phase, the c_p is equivalent to 1.381378 $\frac{kJ}{kgK}$, while after the fusion of the whole body, the c_p , at a temperature of 51.88 ° C, corresponds to 1.486756 $\frac{kJ}{kgK}$.

5.3.2 BUTTER

The second material analyzed for the DSC study is butter. Through this study it was possible to determine the behaviours that the material has taken during the exchange and thermal storage phase carried out in the laboratory.

Also in this case the specific power, expressed in W/g, was obtained when the temperature varies in a range from -20 to 90 °C.

The sample of butter used for the study has a weight of 13.7 mg, which has been subjected for one minute to temperatures of -20 to 90 °C, and then to have a temperature variation, belonging to this range, with a cadence of 10 °C/min.



Figure 117 Result of DSC analysis of the butter

The figure shows both the phases to which the material is subjected. What is mainly evident from the graph, are the peaks that assume the function during the variation of the temperature over time.

The area subtended by the peaks would correspond, both in the melting phase and in the solidification phase, to the underlying heats belonging to the corresponding phases.

As for the charge phase, assumed by the negative values of the function, it occurs between $9.0195 \circ C$ and $48.141 \circ C$. This means that the melting phase of the material takes place at low temperatures and close to those of operation of a thermal storage system. In fact, the latent heat for this interval is about 132.5755 kJ / kg, while that relating to the temperature range recorded in the laboratory, 20 and 52 ° C, is around 100.5795 kJ / kg. This means that when 52 °C is reached, most of the material has completely melted.

Through the use of the Matlab R2015b software it was also possible to obtain the latent solidification heat of the material. This value is equal to 115.9361 kJ / kg and this means that the butter releases heat more or less at the same time interval but at different temperatures.

A characteristic of butter is its composition. In fact, the material is composed of water, which made it difficult not only to record data during the laboratory test, but also during the DSC analysis.

In fact, the test, only for the butter, was carried out twice, obtaining two distinct results.

The choice was then placed with the latest DSC analysis because it takes more truthful and closer to a more realistic case.

The second phase of the DSC analysis was that of obtaining, from the data taken from the test, the specific heat at constant pressure.

By examining the butter and sapphire, it was possible to derive specific heat at the extremes of the melting range of the organic material.

In fact, through the equation previously cited, it was found that in correspondence with the 9.0195 °C, in the solid phase, the c_p is equivalent to 2.367752 $\frac{kJ}{kgK}$, while after the fusion of the entire body, the c_p , at the temperature of 48.141 °C, corresponds to 2.396385 $\frac{kJ}{kgK}$.

5.3.3 PARAFFIN WAX

Paraffin is the most interesting material to be discussed, derived from the DSC analysis. In fact, unlike other materials, paraffin has a very different behaviour, compared to the organic waste materials taken into consideration, despite being the most used material in the field of phase change thermal accumulation.

The paraffin sample used for the analysis has a weight of 10 mg and also in this case a study has been carried out on the material in a time interval ranging from $-20 \degree C$ to $90 \degree C$.

At the extremis of the interval of the study, the material remains at those temperatures for a minute, while in the later stages, the temperature varies at a rate of $10 \degree C/min$.

In this case, unlike the other materials examined, the peaks are highlighted for both phases of the test. The peaks take on much larger values because, both for the charge and discharge phase, the material needs a certain amount of thermal energy much higher than those required by organic waste materials.



Figure 118 Results of the paraffin wax obtained from the DSC analysis

As can be seen from the figure, the material begins its liquefaction phase at a temperature that is around 26.9164 °C and then ends at 62.0494 °C.

Using the Matlab R2015b software it was possible to calculate the area subtended by the curve that would correspond, according to the calculations, to the latent heat of fusion. In this case, the latent heat of melting is equal to 266.9527 kJ/kg. While in the accumulation phase carried out in the laboratory, the temperature range goes from 20 °C to 52 °C reaching a heat of 131.3579 kJ/kg. This value calculated by the software means, that during the phase-change thermal accumulation, even if reaching the temperature values that are consonant for the system's operation, not all the material is liquefied and the maximum quantity of thermal energy is not accumulated.

With regard to the solidification phase, and thus of discharge, the latent solidification heat which affects the entire phase transition phase was recorded.

This range goes from 49.2584 °C to 13.0723 °C obtaining a latent solidification heat value equal to 268.0006 kJ/kg. This last value indicates that both in the charge phase and in the discharge phase, the material needs the same amount of energy because of the crystalline structure with which the body examined is composed.

The final phase of the DSC analysis reproduced on paraffin is the calculation of the specific heat at constant pressure of the material. This last value, obtained analytically, was calculated for the only phase of liquefaction of the material. The calculated data refer to the phase before

and after the material discharge phase, so as to check how much the specific heat varies during the phase transition phase.

Through the comparative study between paraffin and sapphire, it was possible to determine the specific heat of the material examined at the extremes of the range that affects only the fusion phase.

In fact the paraffin wax, in solid phase at the temperature of 26.9164 °C, obtained a c_p of $1.626233 \frac{kJ}{kgK}$.

While after the fusion of the body, in the liquid phase, at the temperature of 62.0494 °C a specific heat at constant pressure was recorded equal to $1.82304 \frac{kJ}{kgK}$.

5.3.4 ANIMAL FAT

The last material studied for DSC analysis is animal fat obtained from a posthumous phase when cooked. This material is the most interesting to analyze because, compared to the previous ones, it is the one obtained from the waste of a previous processing.

The sample examined has a weight of 11.7 mg and has been analyzed, as well as for the other materials, in a temperature range ranging from -20 °C to 90 °C. The material was kept for extreme temperatures for one minute while in the intermediate phases of the analysis the temperature was varied at a rate of 10 °C/min.

From the results of the analyses, it is shown, in the figure 119, that the charge phase, which corresponds to the negative values of the function, consists of two peaks, thus extending the transition phase for a long period.

In fact, the entire liquefaction phase of the material takes place from minus -5.5774 °C to 41.0451 °C, thus obtaining, through the MATLAB R2015b software, a latent melting heat value of 147.4368 kJ/kg.



Figure 119 Animal fat result obtained from DSC analysis

Instead, in the operating temperature range studied in the accumulation phase from 20 to 52 $^{\circ}$ C), reproduced in the laboratory, the latent heat of fusion is equal to 85.6030 kJ / kg.

This means that, even if it reaches high temperature values, the material does not liquefy completely, but it could, however, be used for applications that work at lower temperatures, in order to exploit as much thermal energy as possible.

As regards the solidification phase, a single peak is highlighted throughout the entire function. This sudden increase in the values of the specific power, occurs from 14.9222 °C to -19.9241 °C, reaching a latent solidification heat value of 105.4378 kJ / kg.

Also in this case, it is possible to notice how the phase transition period takes place at low temperatures. This means that the animal fat, recovered from a previous cooking phase, is preferable to use it for thermal applications that work at medium-low temperatures.

The final step of the DSC analysis consists in the analytical calculation of the specific heat at constant pressure for the liquefaction phase only.

Through the DSC study between animal fat and sapphire, the specific heat of the examined material was obtained in correspondence with the extremes of the interval that concerns only the fusion phase. In fact, a c_p of 1.637794 $\frac{kJ}{kgK}$ was obtained from the fat, in a solid phase at a temperature of -5.57735 °C.

While after the fusion of the body, in liquid phase, at a temperature of 41.0451 °C a specific heat value was recorded at a constant pressure of 1.844011 $\frac{kJ}{kaK}$.

6. CONCLUSIONS

The tests carried out in the laboratory have reported some very interesting findings in the use of organic waste materials in the field of thermal storage with phase change materials.

The first step was to verify that certain temperatures reached by the material when in contact with a heat source with a constant temperature.

What we wanted to highlight was that of being able to easily reach temperatures close to those of fusion and that belonged to the operating temperatures of a thermal storage system.



Figure 120 Melted lard obtained during test in the laboratory



Figure 121 Melted paraffin wax obtained during test in the laboratory



Figure 122 Melted butter obtained during test in the laboratory

The figures show how the water placed in the container at a temperature of 60 $^{\circ}$ C, for almost all the tests and for all the materials, makes the material in question melt.

Obviously, not all the body can melt, since in this case the conductive heat exchange between the source and the phase change material is subtracted from the thermal dispersions to which the whole system is subjected.

In fact, through the simulation reproduced by the COMSOL Multiphysics 4.3a software, it has been possible to verify how these thermodynamic losses are reduced compared to that shown by the laboratory tests. In fact, the final temperatures recorded by the laboratory tests have proven lower values than those obtained from the simulation.

From the recordings made, however, it has been possible to verify that the temperatures reached by the material promise excellent prospects of use of the examined organic waste, for possible purposes in the field of thermal storage.

With the scale tests of the thermal storage system, a further layer of PCM was introduced into the system between the water container and the insulator.

This choice was made for a matter of practicality and for an easy removal of the organic material from its container.

Through the tests reproduced in the laboratory it was possible to highlight the thermodynamic qualities of the material if it is in contact with a source of heat.

In fact, through the resistance the water was kept at a constant temperature of about $60 \degree C$ and through this thermal stress it was noticed how the fluid reaches a temperature peak belonging to the operating temperature range of a thermal storage system.

Using the simulation of the COMSOL Multiphysics 4.3a software, it was possible to verify that the same temperature values could be reached within the same time range. Which means that for a possible application in a thermal storage system it is feasible.

Naturally, the differentiation with a common phase change material for an accumulation system means that it can not completely replace the commonly used PCMs.

One of the factors that does not allow the complete use of organic waste materials such as PCM is their easy deterioration.

Therefore, for easy removal, the stratigraphy reproduced in the laboratory was chosen so as to verify its real application in the field of thermal storage.

In fact, by means of laboratory studies, it has been determined that at the end of each individual test, after the phase change phase discharge phase, the water temperature is higher than the ambient temperature.

So the water, after a certain period of time, does not return to the initial conditions. This means that energy savings could be obtained in an entire solar thermal system for a common home for the use of domestic hot water.



Figure 123 Typical solar thermal system with thermal storage and auxiliary system

From the figure shown, a solar thermal system with thermal storage and auxiliary system has been reproduced using Polysun Simulation software in order to clearly visualize how a thermal storage system is positioned inside a domestic hot water production system. It has been hypothesized that the installed storage system has a stratified temperature regime within the volume.

Generally the lowest temperature recorded within the storage system is the ambient temperature that is between 18 and 20 $^{\circ}$ C.

Assuming to be able to calculate the useful energy requested by the user, the following formula was used.

$$\dot{Q}_u = \frac{V \cdot c_p \cdot (T_{user} - T_{mains})}{3600 \cdot 1000}$$
(6)

In this case we know that:

- V corresponds roughly to the volumetric quantity that the user requests for domestic hot water: 50 lt;
- c_p coincides with the specific heat at constant water pressure equal to 4186 $\frac{J}{kqK}$;
- T_{user} is the leaving water temperature used by the user at 45 °C;
- T_{mains} is the water temperature reintroduced in the accumulation and withdrawn from the water network: 15 °C. [44]

Therefore, in this case the thermal energy required for heating the water by the user is equal to 1.744 thermal kWh.

In the case of a possible replacement of a generic accumulation system with one real size with the same stratigraphy studied in the laboratory, it has been hypothesized to obtain as a minimum temperature, T_{mains} , of about 22 °C.

This value was obtained from an average of the final temperature of the water obtained from the laboratory tests (from 23 °C of the test with parchment to 29 °C of paraffin) and 15 °C of the temperature of the water taken from the water network.

Replacing the T_{mains} from 15 °C to 22 °C gives a user thermal energy demand equal to 1.337 thermal kWh, obtaining a percentage reduction of the thermal energy equal to 23.33%.

Through the DSC analysis it has been determined that organic waste materials reach excellent temperature values and that the operating temperature of the domestic hot water system belongs to the melting temperature range of the materials examined.

However, through the analyzes carried out in the laboratories of the Applied Science and Technology Department (DISAT), it has been shown that all the energy that can be accumulated during the melting phase is not completely exploited by the material installed in the thermal storage system.

This does not mean that the material is not applicable for the purposes identified but that, having those operating temperatures, the organic material does not completely melt but can still be exploited to obtain energy savings in the context of the solar thermal storage system.

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