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Integration of high temperature phase change materials in thermal storage systems for advanced energy recovery in industrial furnaces

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INTEGRATION OF HIGH TEMPERATURE PHASE CHANGE MATERIALS IN THERMAL STORAGE SYSTEMS FOR ADVANCED ENERGY RECOVERY IN INDUSTRIAL FURNACES

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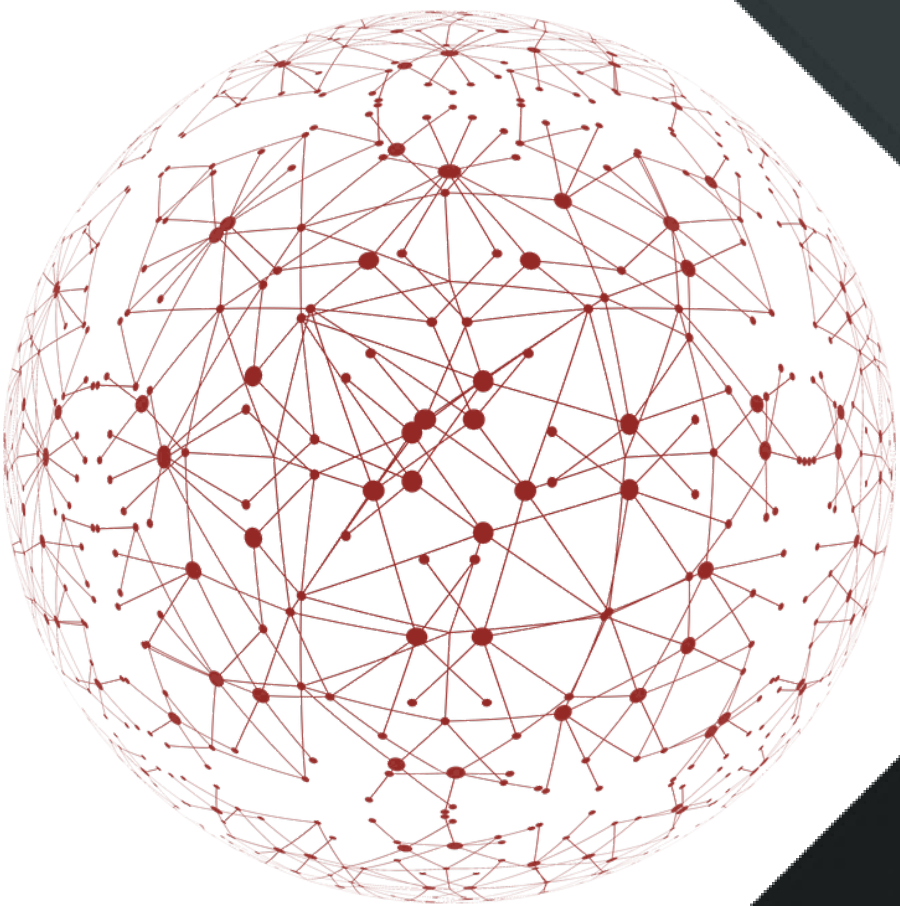

Doctoral Thesis

INTEGRATION OF HIGH TEMPERATURE PHASE CHANGE MATERIALS IN THERMAL STORAGE SYSTEMS FOR ADVANCED ENERGY RECOVERY IN INDUSTRIAL FURNACES

Patricia Royo Gutiérrez

THESIS TITLE:

INTEGRATION OF HIGH TEMPERATURE PHASE CHANGE MATERIALS IN THERMAL STORAGE SYSTEMS FOR ADVANCED ENERGY RECOVERY IN INDUSTRIAL FURNACES

GENERAL OBJECTIVE:

Model, design and analysis of operational behaviour of PCM storage systems at very high temperatures (500-800°C) and their integration in energy-intensive industrial sectors.

DOCTORATE PROGRAMME:

Renewable Energies and Energy Efficiency at University of Zaragoza

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UNIVERSITY TUTOR: Prof. Ignacio Zabalza Bribián

DATE OF PERFORMANCE: Zaragoza (Spain), 1st September 2020

TÍTULO DE LA TESIS:

INTEGRACIÓN DE MATERIALES DE CAMBIO DE FASE DE ALTA TEMPERATURA EN SISTEMAS DE ALMACENAMIENTO TÉRMICO PARA LA RECUPERACIÓN AVANZADA DE ENERGÍA EN HORNOS INDUSTRIALES

OBJETIVO GENERAL:

Modelado, diseño y análisis del comportamiento operacional de los sistemas de almacenamiento de PCM a muy altas temperaturas (500-800°C) y su integración en sectores industriales con consumo energéticos intensivos industriales de alto consumo energético.

PROGRAMA DE DOCTORADO:

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FECHA DE REALIZACIÓN: Zaragoza, 1 de Septiembre de 2020

A mi padre:

Por seguir siempre cerca guiando mi camino,

a pesar del inexorable paso del tiempo,

a pesar de la infinita distancia.

Porque nunca serán suficientes

para dejar de sentir tu cálida presencia.

To my father:

Because time and distance

will never win the battle of memory.

ABSTRACT

The energy considered as waste heat in industrial furnaces owing to inefficiencies represents a substantial opportunity for recovery and storage. Nevertheless, the application of thermal energy storage (TES) systems based on phase change materials (PCM) in energy-intensive industries (EII) at very high temperatures is scarce and restricted by technological and economic barriers. The topic of this PhD thesis is framed on the study and analysis of PCM-TES to be used as a waste heat recovery and storage unit for high temperature applications (up to 1000ºC). The main objective of PCM-TES integration is recovering and storing waste heat from combustion gases or other surplus sources, currently unused, to preheat the air temperature entering the furnace, or other heat demanding processes. In this vein, implementing PCM-TES is a sustainable and innovative option to increase energy efficiency (5-10%) and to reduce the environmental impact associated. The combustion air preheated with the recovered thermal energy reached an increase up to 200-300ºC in the cases analysed in the dissertation.

Design of latent heat TES requires knowledge of the heat transfer process, as well as the phase change behaviour of the PCM used. On the one hand, the configuration design is specifically adapted to the plant operational requirements, by a methodology combining the search of the best conceptual design and a proper PCMs selection. To that end, key technical, energy and economic factors are weighted by an in-house multiple criteria decision analysis (MCDA) to define the most promising design configuration. The final chosen conceptual design consists of a shell-and-tube system, where the exhaust gases flow inside the tubes, the air combustion is placed in the shell side and the PCM is contained in doubled concentric tubes. On the other hand, thermal characterisation and stability cycle tests were performed on the candidate storage materials for two representative application cases in the ceramic and steel industries. Both metal alloys and inorganic salts were analysed to select the most suitable alternative of PCMs working at high temperature.

To investigate the operation of PCM systems, computational simulations can assess the thermal behaviour and expected operational performance. In this sense, temperature profiles of the PCM and the heat transfer fluids are defined by means of 3D numerical model implemented in MATLAB® and COMSOL Multiphysics®. In both models, the energy equation considers both heat conduction and natural convection to predict its effect on the behaviour of the PCM.

The first approach is the MATLAB® in-house-developed modelling of the melting and solidification processes. This tool sets the basis for an appropriate system design and sizing, thermal stress resistance and material selection ensuring the technical feasibility of these systems working at critical temperature ranges. The results are reliable and less time consuming; thus, it is a useful tool during the early design stages and for practical application in the engineering and industry. Specifically, for the ceramic sector, the design resulted in a shell-and-tube system with 1188 kg of a PCM melting at 885ºC involving a latent storage capacity of 227 MJ. In this case, it was demonstrated the achievability of very high temperature levels in the combustion air for preheating (over 700ºC, higher than conventional sensible heat exchangers). Similarly, 1606 kg of PCM, whose phase-change temperature is 509ºC, is considered for the steel sector providing a latent capacity of 420 MJ. The combustion air was preheated from 300 to 480°C, matching the intermittent heat treatment and batch processes of the steel plant.

In the second model approach, the obtained results from the COMSOL Multiphysics® modelling aims at simulating multiphysics problems and allows predicting the thermal performance with high precision; conversely, it presents a higher computational time cost. This model is used to simulate the industrial prototype and to perform a prospective validation of the MATLAB® model. This thesis aims at promoting and facilitating the integration of PCM-TES systems at industrial scale. In this line, technical documentation and process specifications for the PCM-TES prototype were established to achieve the level of reliability, efficiency and safety required. As a result, the configuration of the system was adapted to the plant requirements and the procedures for working operation and the instrumentation of the monitoring and control system were developed. Regarding simulated PCM-TES prototype performance, the combustion air received 338 kWh of heat from the PCM within 3 hours. During the charging, the PCM absorbed 351 kWh from the flue gas stream for 6 hours. In total, the annual energy savings are 230 MWh. The predicted thermal behaviour provides the PCM-TES design validation and reduces the uncertainty risks in the operational performance and its on-site implementation at large scale.

With the aim of proofing the feasibility of a cross-sectorial approach by enlarging its replicability in many industrial sectors, a simplified tool based on the MATLAB® model was developed based on correlations among the most relevant system parameters. Along this line, the thesis conducted a parametric and sensitivity analysis to assess the techno-economic performance of the PCM-TES solution under different working conditions and sectors. This assessment highlighted that a suitable design, material selection and sizing are crucial parameters to obtain energy and economic benefits. Additionally, a multicriteria assessment was conducted with the tool outputs comparing metal alloys and inorganic hydrated PCM salts. Overall, the inorganic PCMs presented NG savings up to 2.6%, which means a higher net economic and energy savings (26,400 €; 480 MWh/year); while metal alloys involved shorter charge/discharge cycles and competitive economic ratios, its commercial development is, conversely, still limited. Finally, acceptable payback periods are observed when operating under 800ºC (between 5-8 years in the steel sector). This fact highlighted the technical and economic barriers existing in working at high temperature levels.

All things considered, this thesis aims at demonstrating the feasibility of implementing, at industrial scale, a PCM-TES system of recover wasted energy from EIIs and overcoming the current lack of information, especially at high temperatures. The results obtained are a starting point for consolidating and promoting novel technological solutions and materials towards a more sustainable and efficient industry.

RESUMEN

La energía considerada como calor residual debido a su ineficiencia representa una oportunidad sustancial para la recuperación y el almacenamiento para los hornos industriales. No obstante, la aplicación a muy altas temperaturas de sistemas de almacenamiento de energía térmica (TES) basados en materiales de cambio de fase (PCM) en las industrias de alto consumo energético (EII) es escasa y está restringida por barreras tanto tecnológicas como económicas. El tema de esta tesis doctoral se enmarca en el estudio y análisis de los PCM-TES para su utilización como sistema de recuperación y almacenamiento de calor residual en aplicaciones de alta temperatura (hasta 1000ºC). El objetivo principal de la integración del sistema PCM-TES es recuperar y almacenar el calor residual de los gases de combustión u otras fuentes excedentes, actualmente no utilizadas, para precalentar la temperatura del aire que entra en el horno u otros procesos que requieren este tipo de energía. En este sentido, la implementación de PCM-TES es una opción sostenible e innovadora para aumentar la eficiencia energética (5-10%) y reducir el impacto ambiental asociado. Concretamente, en los casos analizados en la tesis, el aire de combustión precalentado con la energía térmica recuperada alcanza un aumento de 200-300ºC.

El diseño de los TES basados en calor latente requiere el conocimiento del proceso de transferencia de calor, así como del comportamiento de cambio de fase del PCM utilizado. Por un lado, el diseño de la configuración se debe adaptar específicamente a los requisitos operativos de la planta, mediante una metodología que combina la búsqueda del mejor diseño conceptual. Se ponderaron los factores clave desde el punto de vista técnico, energético y económico, mediante un análisis de decisiones con criterios múltiples (MCDA) en una matriz desasrrollada específicamente para definir la configuración de diseño más prometedora de esta aplicación. El diseño conceptual elegido consiste en un sistema de carcasa y tubos, donde los gases de escape fluyen dentro de los tubos, el aire de combustion dentro de la carcasa y el PCM está contenido en tubos concéntricos dobles. Por otra parte, cabe destacar la importancia de una adecuada selección de los PCM, especialmente en los casos de operación a alta temperatura. Se realizaron análisis experimentales de caracterización térmica y de estabilidad cíclica en los PCM candidatos para dos casos representativos de aplicación: la industrias de la cerámica y del acero. De este modo, se analizaron tanto aleaciones metálicas como sales inorgánicas con el fin de seleccionar la alternativa más adecuada para cada caso y, a su vez, industrialmente viables.

Con el objetivo de investigar el funcionamiento de los sistemas PCM, se utilizaron simulaciones computacionales que evalúan el comportamiento térmico y el rendimiento operacional. En este sentido, los perfiles de temperatura del PCM y de los fluidos de transferencia de calor se definieron por medio de modelos numéricos 3D, implementados en MATLAB® y COMSOL Multiphysics®. En ambos modelos, tanto el efecto de calor por conducción como la convección natural se han considerado en la ecuación de energía para predecir su efecto en el comportamiento del PCM.

El primer enfoque es el modelado customizado de los procesos de fusión y solidificación desarrollado en MATLAB®. Esta herramienta sustenta las bases para el dimensionamiento y diseño del sistema, resistencia al estrés térmico y selección de materiales, asegurando la viabilidad técnica de estos sistemas trabajando en rangos de temperatura críticos. Los resultados alzanzados son fiables y requieren un bajo coste computacional; por lo tanto, representan una herramienta útil para las primeras etapas de diseño y para la aplicación práctica en ingeniería e industria. Concretamente, para el sector de la cerámica, el diseño seleccionado consiste en un sistema de tubo y carcasa, integrando 1188 kg de un PCM que funde a 885ºC, que supone una capacidad de

almacenamiento latente de 227 MJ. En este caso, se demostró la posibilidad de alcanzar niveles de temperatura muy elevados en el aire de combustión para el precalentamiento (más de 700ºC, temperatura por encima de la conseguida en los intercambiadores convencionales de calor sensibles). Del mismo modo, para el sector del acero, se consideraron 1606 kg de PCM, cuya temperatura de cambio de fase es de 509ºC, que proporcionan una capacidad latente de 420 MJ. El aire de combustión se precalentó de 300 a 480ºC, lo que se corresponde con los procesos de tratamiento térmico intermitente y por lotes de la planta siderúrgica.

En el segundo enfoque, el modelo en COMSOL Multiphysics® se utiliza para simular problemas de multifísica y predecir el rendimiento térmico con gran precision; por el contrario, presenta un mayor tiempo de cálculo. Este modelo permite simular el prototipo industrial y realizar una validación prospectiva del modelo MATLAB®. Esta tesis tiene como objetivo promover y facilitar la integración de los sistemas PCM-TES a escala industrial. En esta línea, se establecieron la documentación técnica y las especificaciones de proceso del prototipo PCM-TES para lograr los niveles de fiabilidad, eficiencia y seguridad requeridos. Como resultado, la configuración del sistema se adaptó a los requisitos de la planta, y se desarrollaron los procedimientos para el funcionamiento y la instrumentación del sistema de monitorización y control. El rendimiento del prototipo PCM-TES se evaluó simulando procesos de carga y descarga. En el proceso de carga, el PCM absorbe 351 kWh de la corriente de gases de combustión residuales durante 6 horas. Durante las descargas, el PCM aporta 338 kWh de calor al aire de combustión durante 3 horas. En total, el ahorro anual de energía es de 230 MWh. Los resultados obtenidos del comportamiento térmico proporcionan una validación teórica del diseño del PCM-TES y reducen el riesgo de incertidumbre durante la operación y la implementación in situ a gran escala.

Adicionalmente, se desarrolló una herramienta simplificada a partir de correlaciones entre los parámetros más relevantes del sistema y basada en el modelo MATLAB®, con el fin de investigar su viabilidad y replicabilidad con un enfoque intersectorial. Se realizó un análisis paramétrico y de sensibilidad para evaluar el rendimiento tecno-económico de la solución PCM- TES en diferentes condiciones de operación y en distintos sectores industriales. Esta evaluación reveló que un diseño, una selección de materiales y un dimensionamiento adecuados son parámetros cruciales para obtener beneficios energéticos y económicos. Además, se llevó a cabo una evaluación multicriterio con los resultados de la herramienta, comparando las aleaciones metálicas y las sales inorgánicas hidratadas. En general, los PCM inorgánicos presentaron un ahorro de gas natural de hasta 2.6%, resultando en un mayor ahorro económico y energético neto (26,400 euros; 480 MWh/año). Por su parte, las aleaciones metálicas implicaban ciclos de carga/descarga más cortos y ratios económicos competitivos, por el contrario, su desarrollo comercial es aún limitado. Por último, se observaron períodos aceptables de recuperación de la inversión (entre 5 y 8 años en el sector del acero) cuando se opera a menos de 800ºC. Este hecho pone en relieve las barreras técnicas y económicas existentes que todavía limitan la integración de PCM en las operaciones a alta temperatura.

En definitiva, la presente tesis doctoral pretende demostrar la viabilidad de implementar, a escala industrial, un sistema PCM-TES de recuperación de la energía térmica residual de las industrias intensivas y superar la actual falta de información, especialmente en su aplicación a altas temperaturas. Los resultados obtenidos representan un punto de partida para consolidar y promover soluciones tecnológicas y materiales innovadores hacia una industria más sostenible y eficiente.

To climb a ladder, ou don't have to see the whole staircase, just take the first step.

Martin Luther King Jr.

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One good turn, deserves another.

This thesis would not have been possible without the excellent guidance and support of my supervisors, Dr. Germán Ferreira and Dr. Ana María López. I am very grateful to them for their priceless time, dedication and constructive discussions. They taught me with passion and selflessly shared their experience with me, leading the first steps of my professional career during these six years. You achieved to find the exact point where high-level professionalism and the kindness of a friend meet. Hence, I would like to honestly thank them both, not only for the thesis, but for encouraging my investigation and allowing me to grow as a research scientist and a person.

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The thesis is a metaphor of life in miniature where people, events, experiences, successes, failures and sudden pandemics occur; where you experience frustration against obstacles or helplessness in the face of unsolvable problems. But you can also feel the courage to face them, the sacrifice and effort invested, the relief and satisfaction of overcoming them. Even what you least expect, it gives you a valuable insight. It is in your hand to use it to your own advantage.

Patricia Royo

LIST OF ABBREVIATIONS AND SYMBOLS

A	Heat exchange area; or Aspect ratio
a_m	Extent of conversion or reaction fraction
AHP	Analytical Hierarchy Process
α	Thermal diffusivity
BAT	Best Available Techniques
BDF	Backward Differentiation Formula
β	Thermal expansion coefficient
c	Fixed costs
ca, *comb.air*	Combustion air
c_p	Specific heat
COMAH	Control of Major Accident Hazards
CPC	Cooperative Patent Classification
CTE	Coefficient of Thermal Expansion
D	Diameter
DOF	Degrees Of Freedom
DP	Drop Pressure
DSC	Differential Scanning Calorimeter
DTA	Differential Thermal Analysis
∂t	Time variation
ΔH	Variation of enthalpy
ΔH_{latent}	Enthalpy of fusion or vaporisation
ΔH_r	Enthalpy change for the reaction
$\Delta L / L_o$	Degree of expansion
Δt	Time step
ΔT	Variation of temperature
Δx, Δy, Δz	Length step in cartesian coordinates
E	Energy
e	Thermal effusivity
EII	Energy Intensive Industry
EU	European Union
$\bar{\in}$	Mean convective enhancement factor
f, f_L, *LF*	Liquid phase fraction
FDM	Finite Differences Method
FEM	Finite Element Method
fg	Flue gases, exhaust gases
Fo	Fourier number
FoF	Factories of the Future
FTCS	Forward-Time Central-Space
g	Gravitational acceleration
GDP	Gross Domestic Product
GHG	GreenHouse Gas
GOP	Gauge Operating Pressure
Gr	Grashof number

GW	General Weight
h	Convection coefficient
H	Latent heat of fusion
H	Heigth
HELP	High Level Expert Panel
HTF	Heat Transfer Fluid
HX	Heat eXchanger
IC	Investment Costs
IEA	International Energy Agency
IPC	International Patent Classification
K	Calorimetric constant
k	Thermal conductivity
k_{eff}	Effective thermal conductivity (conduction and convection)
L	Length
LFA	Laser Flash Analysis
LHS	Latent Heat Storage
LVDT	Linear Variable Displacement Transducer
M	Force
m	Mass
$m_{comb.air}$	Combustion air flow
MCDA	Multiple Criteria Decision Analysis
MRP	Most Relevant Parameters
MSDS	Material Safety Data Sheet
MTPS	Modified Transient Plane Source
M&CS	Monitoring and Control System
n	Number of moles
Nu	Nusselt number
NEI	Net Energy Input
NG	Natural Gas
NIST	National Institute of Standard and technology
η	Efficiency or yield
η_{CH}	Effective charging ratio
η_{DCH}	Effective discharging ratio
O.T.	Maximum operating temperature
P	Volumetric density
PCM	Phase Change Material
PCT	Phase Change Temperature
PID	Process and Instrumentation Diagrams
PPE	Personal Protection elements
Pr	Prandtl number
Q	Heat demand, thermal energy
Qs	Heat stored
Q_{PCM}	Thermal energy transferred by the PCM-TES system
ρ	Density
R	Heat transfer rate for conduction
R^2	Correlation coefficient

R_f	Fouling factor
Ra	Rayleigh number
RANS	Reynolds-Averaged Navier-Stokes
Re	Reynolds number
RW	Relative Weight
S_b	Heat flux boundary condition
SG	Syngas
SHS	Sensible Heat Storage
SPIRE	Sustainable Process Industry through Resource and Energy Efficiency
St	Stefan number
T	Temperature
t	Time
t_{CH}	Time during the charge phase
t_{DCH}	Time during the discharge phase
T_{ini}, T_{fin}	Initial/Final temperature of the time interval
T_{pc}	Temperature of phase-change
TCM	Thermo-Chemical Materials
TGA	Thermo-Gravimetry Analysis
TES	Thermal Energy Storage
TLS	Transient Line Source
TMA	Thermo Mechanical Analysis
TPS	Transient Plane Source
TRL	Technology Readiness Level
τ_f	Fourier number for the liquid fraction (*f*) calculation
$\bar{\tau}$	Scale dimensionless melting time
δ	Thickness
U	Internal energy
U	Global heat transfer coefficient
V	Volume
v	Velocity
ν	Kinematic viscosity
μ	Dynamic viscosity
W	Width
WHR	Waste Heat Recovery
∇	Nabla operator $= (\partial/\partial x, \partial/\partial y, \partial/\partial z)$

«Reserve your right to think, for even to think wrongly is better than not to think at all.»

Hipatía de Alejandría

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«Un país sin investigación es un país sin desarrollo»-Sin ciencia no hay futuro.

Margarita Salas

1 - INTRODUCTION

1.1 World energy and environmental outlook

During the last century, the progress in science and technology fields has enhanced the life quality and increased the world energy consumption, mainly in industrialised countries and emerging economies. Thus, consumerism and population growth have led to an increasing demand for natural resources, energy and raw materials [1, 2]. Especially, the energy demand has significantly increased because of use in sectors such as industry, transportation, construction, and electric generation. For years, fossil fuels and nuclear energy have been dominant sources of energy [3]. However, this increase in energy consumption leads to significant environmental impacts such as the depletion of resources and the growth of gas emissions to the atmosphere, among others. Since all countries suffer the harmful consequences, this is considered a global problem, and it must be faced as such. Therefore, the current model of energy production should be substituted for a more sustainable model to reduce energy and material consumption.

The European Commission has proposed numerous strategies towards "Europe 2020" over the last decade [4], in order to create the conditions required for smart, sustainable and inclusive growth. Specifically, many of them are focused on the climate objectives towards a low carbon economy, the internalization of the environmental costs of energy and the creation of an energy system that guarantees affordable energy for all consumers, which increases the security of the energy supply of European Union and reduce our dependence on energy imports. These actions are included in the framework on climate and energy for 2030, whose main objectives are three: at least 40% reduction of greenhouse gas (GHG) emissions compared to 1990; at least 27% share of renewable energy and at least 27% improvement in energy efficiency. In the long-term, the European roadmap for the year 2050 [5] establishes a reduction of emissions to 80% compared to 1990, where all sectors should contribute based on their technological and economic potential.

At present, numerous initiatives aim at boosting the performance guidelines in order to meet environmental targets [6]. Consequently, these growing environmental, social and economic requirements lead the industries towards reengineering and retrofitting challenges meant to increase productivity, cost-effectiveness, energy and resource efficiency and eco-innovative designs [7]. Among them, the energy generation and the industrial sector present the greatest reduction potential, as it is shown in Figure 1 [8].

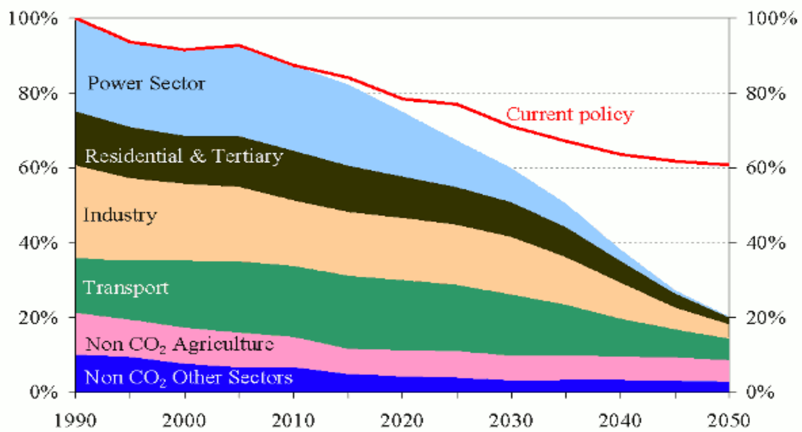

Figure 1. Evolution of GHG emissions distribution by sector and European roadmap up to 2050 [8].

Energy-intensive industries (EII), including sectors such as chemicals, steel, aluminium, mining, cement, glass, ceramics, paper and pulp, are responsible for great environmental, economic and social impacts. For example, about 54% of the world's total energy was used in industrial sectors [9] and the world power demand represented around 60 billion MW in 2015 [10]. Besides, it must be considered the impact of the energy crisis and the research, development and advocacy for new innovative alternatives to reduce the use of fossil fuels, in order to avoid economic and political dependence of the countries who own the reserves.

1.2 Challenges and opportunities in the energy-intensive industry

1.2.1 Current industrial situation

The EII plants operating in European and national territory are continuously facing critical challenges stemming from the previously stated objectives. Several strategies such as management, technologies and policies have been reported to improve the energy efficiency and decarbonising the industrial sector over the past years [10-12]. These actions are also relevant to accomplish the objectives of the UNE-EN ISO 50001 standard, which has managed to generate systematic savings for organisations of between 5% and 30% of energy costs [13]. In particular, the integration of energy transformation and recovery is emphasised to avoid unnecessary entropy production, while causing the production processes to be more cost-effective and environmentally friendly [14]. This concept approach of integration, flexibility and symbiosis is defined as smart energy system, according to Lund et al. [15].

The iron and steel sectors have been pioneers by proposing and implementing a wide range of practices and technologies not only alongside Europe but also worldwide [15]. Already in the 19th century, iron and steel industries developed and installed techniques of waste energy recovery [16]. Furthermore, Beer et al. [17] reported that global energy efficiency in the steel sector would be improved near 30% by 2020, only using existing technologies. Furthermore, the implementation of energy efficient measures was further extended to other sectors. Overall, the European industrial sector has successfully decoupled its performance in terms of value added from the energy consumption, improving its energy intensity by almost 19% between 2001 and 2011 [18]. In fact, Worrell et al. [19] gathered many examples applied to the industrial sector, such as improved technologies and processes, conversion to cogeneration and fuel switching to increase the efficiency, reliability and flexibility of their processes. To this end, the key actions are focused on implementing clean energy policies, renewable energy integration, switching to alternative fuels, removing carbon dioxide from the atmosphere by means of sequestration, developing advanced materials, integrating energy storage and adopting the superior available technologies [20, 21], all under a lifecycle product approach.

1.2.2 Renovation and retrofitting actions

These actions are focused on addressing radical improvements in the competitiveness and energy, environmental and cost performance, which can be implemented at component, process, system, and organizational level [22]. However, these changes disrupt the production or require sometimes high investment or an in-depth renovation process [23]. Thus, industrial plants must assess whether adapting traditional and existing facilities by retrofitting strategies or implementing new technologies with enhanced performance. In this context, the ultimate decision between a new or retrofitted furnace must be well assessed considering the cost-effectiveness and limitations. A retrofitting action should be carefully weighed against the benefits and costs of new equipment that incorporates the most energy-efficient technologies available or eco-innovative designs considering the whole lifecycle from a very early stage.

On the one hand, energy and resource-efficient designs and eco-innovative thinking foster the sustainable development and green transformation. These approaches offer an opportunity for building new equipment and infrastructure with the best available technology and improved performance. However, it requires high investment as well as an in-depth renovation process. Manufacturing plants are long lasting, offering few opportunities for upgrades to the energy efficiency of the core process [24]. This constraint may be overcome by means of retrofitting strategies based on the refurbishment of existing equipment. On the other hand, retrofitting is regarded as a profitable alternative; nevertheless, the performance of these actions is not always possible [25]. There are restrictions regarding the lifespan of the rest of the unchanged components or is limited by the space available for a larger structure [26]. Even so, retrofitting actions can help the industries to accomplish the global commitments towards energy efficiency and low carbon production strategies [27], without compromising their production rates and economic balance. Hence, it is worth noting the numerous benefits of a proper retrofit strategy, which can be summarised as:

- The optimization of already existing plant components and global performance.
- The adaptation of the plant for manufacturing new or modified products.
- An increase in the production rate or a decrease in the processing time.
- Improvements in the energy and material resources efficiency and minimization of losses.
- A reduction in environmental impacts.
- An achievement of important cost savings.

At this point, an important lack of information is found concerning the possibilities of rebuilding and retrofitting of energy-intensive industrial systems. The cause of this scarcity might stem from the differences along the existent equipment types, most of which are non-standard or custom-designed, requiring large efforts to perform upgrading the processes [27]. Thus, benefits and costs must be thoroughly assessed in order to identify the most profitable and efficient alternative.

1.2.3 Waste heat recovery opportunities

One of the critical focuses are the industrial heating systems; in particular when speaking about the feasibility of using alternative energy sources, enhancing insulation and refractory materials and eco-efficient heat recovery systems. Applying the best available technology can involve a 25% decrease in the energy intensity in the industry; even more, an additional 20% can be achieved through innovative systems [15]. Nevertheless, despite the efforts to change the current trend, the International Energy Agency (IEA) [28] reports that industry is half as energy efficient as it could be according to the thermodynamic laws. The average thermal efficiency for installed industrial furnaces is approximately 60% [29], which represent a significant opportunity for improvement by reducing the main causes of heat losses in industrial furnaces, namely leaking of exhaust gases, poor insulation and inefficient performance of combustion parameters.

Within this context, industrial manufacturing plants are highly appropriate for integrating technologies for waste heat recovery (WHR). Furnaces heated by the combustion of hydrocarbon fuels; that is, natural gas, exhibit important heat losses in flue gases (with an average value of 40%, although very poor performances may increase the heat losses up to 70%) [30]. They include a very wide variety of equipment encompassing the range from the smallest laboratory ovens

(1 kWh) up to the biggest cement kiln consuming up to 0.61 TWh of primary energy per year [31]. In Europe alone, this heat recovery potential has been estimated as more than 300 TWh per year [32], which would imply a reduction of 250 million tonnes of CO_2 emissions per year.

Currently, during the industrial operation, large amounts of thermal energy are lost every day in the industrial sector, especially in processes running at medium or high temperatures [33]. An important amount of high-grade energy (>300°C) is dismissed through furnace outputs, such as, the final product, by-products or emitted gases. Figure 2 depicts the energy consumption and process temperatures for the most relevant industrial sectors [34]. The chemical, textile, sugar, paper and pulp industries operate usually at low and medium temperatures. Conversely, most of the EII such as non-ferrous metal, iron, steel, refractories, glass and ceramics work at higher temperatures, over 600°C and even up to 1600°C. This energy considered as waste heat in industrial furnaces owing to inefficiencies represents a substantial opportunity for recovery and reuse to improve the energy efficiency and reduce the environmental impact.

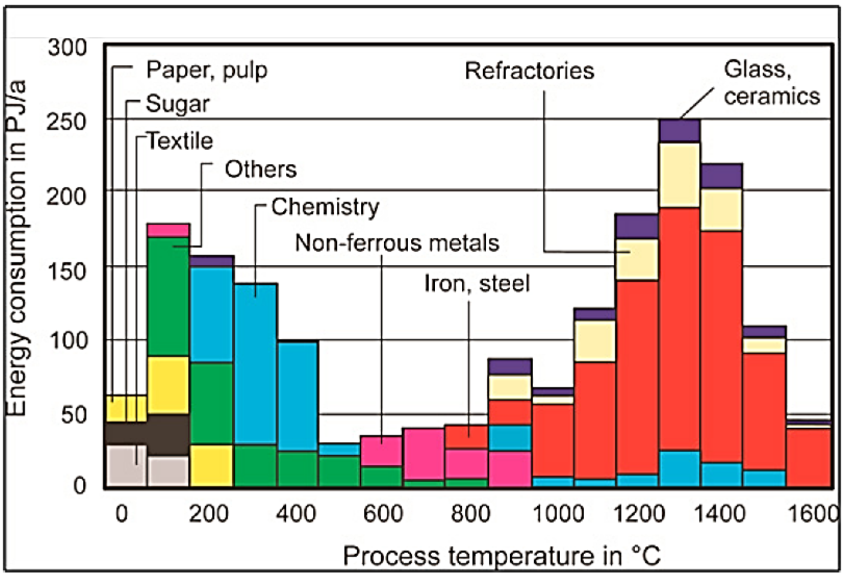

Figure 2. Energy consumption and process temperatures for different industrial sectors [34].

For all these reasons, it is justified that the recovery and storage of energy is framed within the priority lines established in the present and future European Roadmaps to achieve a climate-neutral EU by 2050; as either a new integrated or a retrofitting element for recovering waste heat in EII. Consequently, both the primary fuel consumption and environmental impact can be reduced [35]. For instance, Europe 2020 Strategy, Low-carbon economy and Energy Roadmap 2050 [4, 5, 8] and European Green Deal [36] contain a wide range of measures to promote an energy mix based on renewable energies, to advance in the sustainability of transport, to lead a sustainable, efficient and circular industrial model, to decarbonize the energy sector thanks to the modernization of infrastructures and the promotion of energy efficiency, to reduce the environmental impact by taxing fossil fuels, etc.

Among the measures of energy efficiency and sustainability emerges the thermal energy storage (TES), a technology to harness and manage thermal energy, i.e. by incorporating phase change materials (PCM). The integration of this technology within the industrial heating systems is currently in the research and development phase, as there are many aspects to be improved until its implementation at industrial scale.

1.3 Strategic context research

Regarding the current competitive environment of the EII and their needs, it is described in this section the organized, selective and permanent process that has been developed before and during the thesis. This process makes possible to obtain valuable information on the latest technical developments, thus enabling to follow the latest scientific and technical advances in technology, reduce risks associated with project activities and identify a new and interesting market opportunity. This process can be summarised in Figure 3 and developed in the following sections.

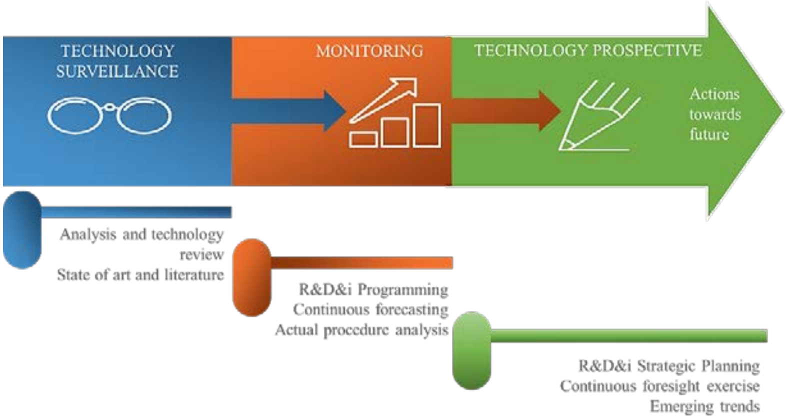

Figure 3. Preliminary phases to the thesis development and evaluation of the research potential.

1.3.1 Technological surveillance and monitoring

Among the possible solutions, the integration of TES stands as a promising option due to its flexibility, which allows adjusting production and demand. Just as gasoline or natural gas is stored in tanks for use when needed, thermal energy can be accumulated and used at times of peak demand. Heat can be stored in three different ways, either as sensible heat (increasing the temperature of the medium chosen to store it), as latent heat (causing a specific material to change state), or by using heat to favour a reversible chemical reaction. Figure 4 represents the technological portfolio of thermal storage based on its current degree of maturity as well as the potential and capacity of these technologies.

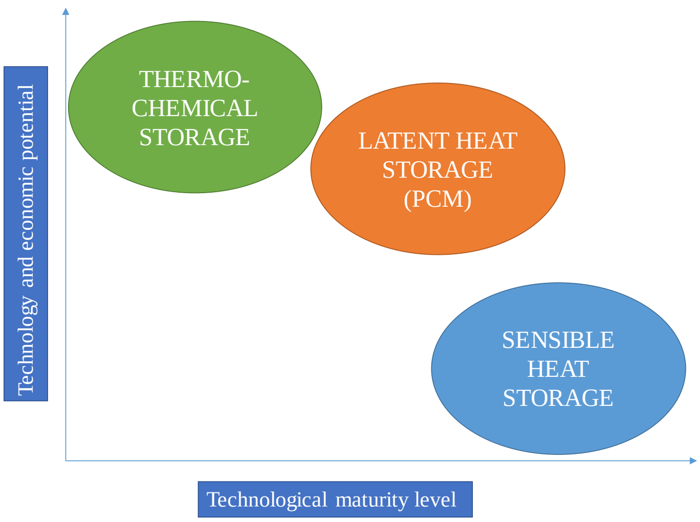

Figure 4. Technological portfolio of thermal storage according to its degree of maturity and potential.

So far, sensible heat storage is the most widely used on the market by increasing temperature in fluids or transfer fluids (HTF). This has been the case thanks to the existence of greater knowledge and control of these processes, which makes its design and construction easier and commercially available. Compared to conventional systems based on sensitive heat transference, they are simple and inexpensive, but require a large amount of storage material and valuable space, latent heat storage (LHS) systems based on PCM have an attractive option to establish advanced TES technologies. The PCM system aims to take full advantage of heat going through the flue gases in order to improve the current energy thermal system from the facility, which has reached a technological limit using commercial solutions at high temperatures [37]. The PCM-TES systems can provide a much higher waste energy storage density and then release it to different industrial applications with a smaller temperature difference. Its use would allow reducing the size, operational failures, environmental impact, and manufacturing and operating costs of several industrial systems that cannot manage the waste generated during their operation.

A PCM is any compound that changes state, either from solid to liquid, from liquid to gas or vice versa. These materials are considered passive and intelligent, because when they reach their phase change temperature, they absorb or release energy in the form of latent heat, maintaining their temperature constant and favouring the transfer of heat [38, 39]. On the other hand, the latent heat of fusion is much greater than the sensible heat, and therefore significantly increases the storage capacity [40]. As a result, a coupling between production and demand is achieved, as well as a reduction in the volume of the system.

However, there are still numerous technological and non-technological barriers that demand significant efforts from the scientific community (Figure 5). The current trend is in the improvement of the design of the storage matrix, optimizing its dimensioning, the layout and number of the load tubes, the design of systems for adequate control of the loads and discharges, increase of the conductivity and the ratio of transfer, etc.

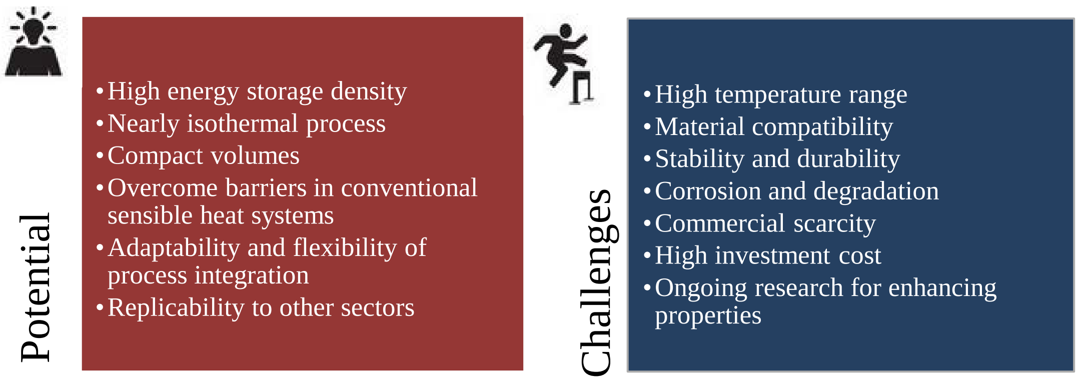

Figure 5. Existing challenges to overcome and potential identification of PCM as TES.

According to the state of the art, several authors, among which Du et al. [41], Abdin et al. [42] and Zalba et al. [43], explore the numerous applications of PCM. In these reviews, PCMs act as regulators and/or thermal storage systems in many science fields, such as electronics, solar energy, construction, refrigeration, textiles, transport and in industrial processes [35, 44].

The evolution of the number of publications of 2010 (3700 articles) to 2019 (16700 articles) shows that interest in this type of PCM-based solutions for thermal storage has increased exponentially in the last decade (Figure 6). Despite PCM-TES application has been studied at low temperatures, medium and high temperatures, there are currently several limitations that hinder its application. However, there are scarce commercial solutions based on high temperature PCM available in the market or implemented on an industrial scale. During the analysis of the research literature, only 10 research papers on PCM operating above 600°C were found at the beginning of the thesis period.

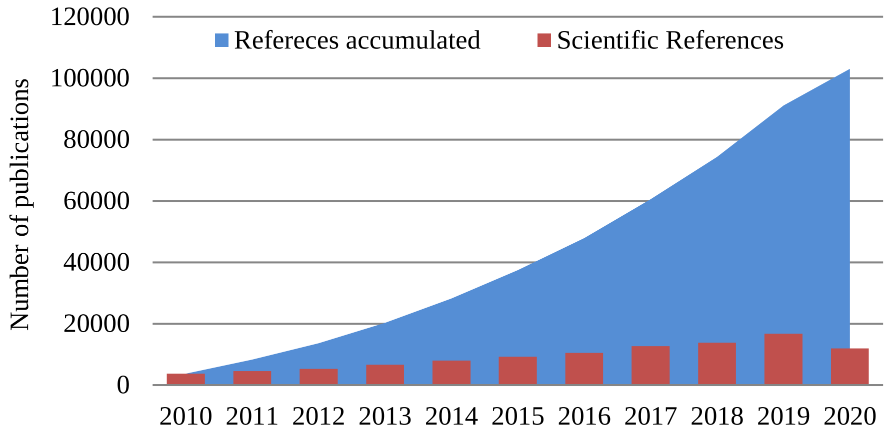

Figure 6. Evolution of PCM article scientific references accumulated in the last decade in Elsevier.

The investigation of patents related to the storage by latent heat by means of PCM allows to obtain two conclusions. The first one is the interest that this issue arouses in the scientific community in different lines. Next, the main fields are shown in Figure 7, according to the code of cooperative patent classification (CPC) [1] based on the international patent classification (IPC)[2]:

- Y02E - Technologies or applications for mitigation or adaptation against climate change related to energy
- F28D - General heat-exchange apparatus
- C09K – Miscellaneous material for different applications
- F28F – Heat-exchange and heat-transfer apparatus
- F25B - Refrigeration machines, plants or systems; combined heating and refrigeration systems; heat-pump systems
- Y10B - Technologies or applications for mitigation or adaptation against climate change related to building

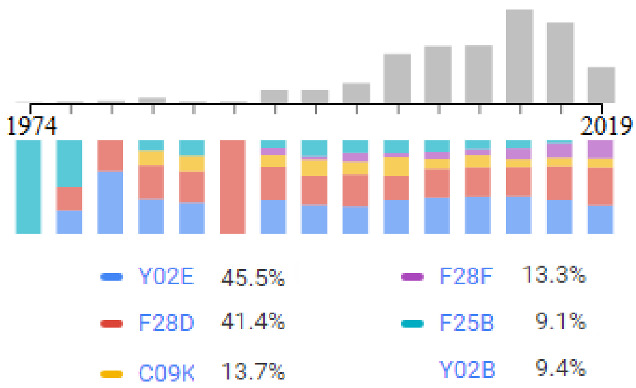

Figure 7. Patent trends related to PCM-TES, sorted by categories (CPC).

[1] Research in Google Patents and Espacenet
[2] rs.espacenet.com

During the last three decades the development of patents in this field has constantly increased, having a greater impact on the ones between 2007 and 2015. Currently, developed patents are mostly considered within the category Y02E of technologies or applications for mitigation or adaptation against climate change related to energy and in category F28D of general heat-exchange apparatus. This data highlights its alienation with the actions and main objectives of Spain, Europe and globally. Notably, the development of patents in this field has increased in companies such as Ford Global Technologies, Kimberly-Clark Worldwide and Rubitherm.

The second conclusion drawn is the possibility of obtaining a patentable result. Most patents are based on PCM manufacturing and synthesis methods, their encapsulation, design and construction of storage systems, as well as their interaction with adjacent materials. On the contrary, it highlights the absence of systems capable of recovering heat at high temperatures.

1.3.2 Prospective: Strategic analysis of the environment (PESTLE)

The PESTLE analysis is an instrument of the general model analysis of context, planning and strategic positioning of a company, project or research line. The acronym PESTLE refers to those political, economic, social, technological, legal and ecological factors that may have some type of influence on the research. The medium in which it is immersed will condition the organisation, its adaptation taking advantage of the opportunities and compensating for its threats. In this way, the impact of those external factors is examined in Table 1, but they become key factors, being able to determine the success or failure in the future implementation of the innovative strategy.

Table 1. PESTLE analysis of the PCM-TES integration.

POLITICAL
The political initiatives have positively promoted the adoption by the market of innovative solutions such as PCM systems. With the roadmaps of Sustainable Process Industry through Resource and Energy Efficiency (SPIRE) and Factories of the Future (FoF), as well as financing systems and grants at local, national and international level, which should be considered from the perspective of the target segments. Besides, the growing political uncertainty in the European Union (EU) and in the world constitutes a possible political barrier.
ECONOMIC
Currently, moderate economic growth in Europe affects the business activities of target sectors, thus reinforcing international competition and offering new opportunities to take advantage of emerging markets with high gross domestic product (GDP) growth rates. Taking into account its innovation, the solution with PCM systems has the potential to break not only in European markets but also in Asia and the Pacific, which present a high demand for energy efficiency technologies and process optimization. On the other hand, the costs and prices of the PCM system are a non-technical barrier to be considered. Fluctuations in energy prices (especially fossil fuels such as natural gas) have a great impact, which is expected to continue in the medium and long term. Therefore, fuel savings and reduced operating costs achieved through the integration of these systems are fundamental economic factors for end users Finally, profitability and financial viability are factors that play an essential role in the decision-making process. Additionally, emission costs and fuel costs in EIIs are expected to vary in the medium and large term during the decarbonisation era, then the variability of renewable energy sources should be also considered. Anyhow, the application of energy efficiency actions reduces the uncertainty of these costs by improving the economic viability of investments.
SOCIAL
The growing need to improve efficiency and the search for sustainability encourage the adoption of new technologies and materials for production processes. In addition, the increase in environmental awareness in society forces companies to improve their public image through the application of energy efficiency technologies. The proposed solution will be able to satisfy

this demand due to its strengths. Despite this, some customers may present non-technical barriers due to the reluctance to new unknown technologies, security problems and brand loyalty. Finally, both the possibility of creating new jobs dedicated to the design, construction and consulting of this new technology, as well as economic growth and an increase in market share can positively boost the end-user to implement a PCM system to industrial level.
TECHNOLOGICAL
The adaptability to the processes in different industrial sectors and the ease of combination with the current production line and R&D can positively affect the integration of the PCM system. We must also consider the technical barriers due to the level of quality, efficiency and availability of PCM at high temperatures. At the same time, end users must deal with problems of maintenance, possible corrosion and charging/discharging times, etc. Finally, the overall reliability and efficiency of the PCM solution play a fundamental role in the decision-making of all the target segments and, therefore, must be addressed along with other technical barriers.
LEGAL
Customers must comply with the respective codes and standards related to the industry in terms of pollution, as well as health and safety standards, which vary at European, national and international level and must be addressed by specific strategies for each geographic market. In addition, certain requirements for the protection and commercialization of intellectual property must be considered. Finally, compliance with the Best Available Techniques (BAT) for combustion plants, to ensure that the PCM system follows the highest standard in the industry.
ENVIRONMENTAL
The evidence of climate change and the depletion of fossil fuels projected for 2075[3] are the main environmental factors that promote strong European efforts to meet environmental goals. The COP21/CMP11 Agreement is the main regulatory framework that affects the macro environment of the PCM system. In addition, national environmental policies and CO_2 regulations must be addressed for each location. On the other hand, the specific legislation on ecological design of industrial thermal systems is the one that will mark the requirements to be met; for example: Industrial Emissions 2010/75/EU[4], Emissions Rights Trade System 2003/87/EC[5], Energy Efficiency 2012/27/EU[6], Ecodesign 2009/125/CE[7].

1.4 Motivation and purpose

The main conclusions of the previous sections are, on the one hand, to reinforce the great potential of the PCM in this field as a storage and thermal management system, where the current energy recovery systems have reached their technological limit through the use of conventional commercial solutions. On the other hand, it is worth highlighting the lack of experimental studies addressing the operation and overall performance of these facilities under real industrial operating conditions, especially at high temperatures. Therefore, the thesis motivation is based on the need to break the barriers, both technical and non-technical, of PCM-TES technology implementation by developing suitable designs and simplified tools supporting its industrial deployment.

[3] www3.nd.edu/~jott/Measurements/Measurements_lab/E4/worldFossilReserves.pdf
[4] European Commission, (2010). DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast) Official Journal of European Union; eippcb.jrc.ec.europa.eu/reference/BREF/LCP_FinalDraft_06_2016.pdf
[5] European Commission, (2003). DIRECTIVE 2003/87/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 13 October 2003 establishing a scheme for greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC. Official Journal of the European Union
[6] European Commission, (2012). DIRECTIVE 2012/27/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 25 October 2012 on energy efficiency, amending Directives 2009/125/EC and 2010/30/EU and repealing Directives 2004/8/EC and 2006/32/EC. Official Journal of the European Union
[7] European Commission, (2009). DIRECTIVE 2009/125/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 establishing a framework for the setting of ecodesign requirements for energy-related products (Recast) (Text with EEA relevance). Official Journal of the European Union.

To this end, the motivation of the proposed solution is aligned with the key actions, in national and international strategies, such as the European roadmaps for the year 2050 [5] and SPIRE [45], as shown in Figure 8.

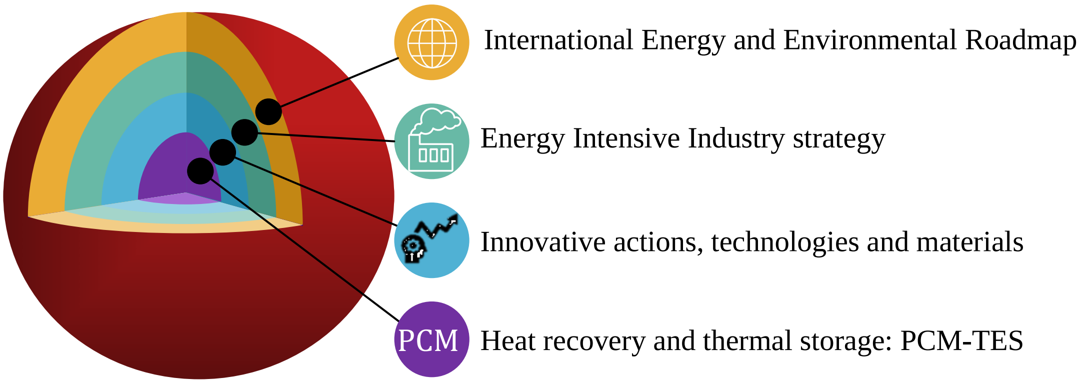

Figure 8. Project motivations and alignment with the roadmap key actions.

In this light, the thesis purpose supports the successful design and integration of novel PCM-TES systems in EII at high temperature ranges for thermal recovery and heat storage. The proposed PCM-TES solution is expected to improve the energy and environmental performance of thermal energy recovery and storage systems, making this thesis a reference framework that validates, both qualitatively and quantitatively, how innovative and sustainable actions generated from the needs in EII sectors. Another advantage of using PCM is the fact that they have smooth the temperature profile at the outlet of the system. This smoothing effect provides a high-quality signal to feed monitoring and control systems, which facilitates the design of upstream and downstream equipment and its integration towards an industry 4.0.

In summary, the line of research that addresses the thesis proposes promising alternatives based on the use of new advanced technologies for the storage and reuse of energy (TES). In addition, innovation in advanced materials (PCM) and design alternatives will contribute to increase the efficiency and performance of industrial processes, reduction of fossil fuel consumption and the use of residual thermal energy, which are key factors for the energy and industrial sector.

1.5 Objective

1.5.1 General objective

The overall objective of the thesis is the design and integration of the new PCM-based TES, which is schematically illustrated in Figure 9, along with the deployment a simplified, robust and verified tool to boost its application in the industrial sector. To do so, the proposed solution aims at recovering the thermal energy at high temperature from an off-gas or surplus from a fossil fuel fed furnace installed in an EII industry. Therefore, that stored energy can be later used for increasing 100-200ºC the current temperature reached in the air combustion flow, and thus achieving and increase around 5-10% of the overall efficiency of the system. In the EII sectors, this accumulated heat could serve to preheat the combustion air going to the furnace inlet, to increase the initial temperature of the load, to keep the products at a constant temperature for heat treatments or in drying processes, among many other upstream and downstream processes.

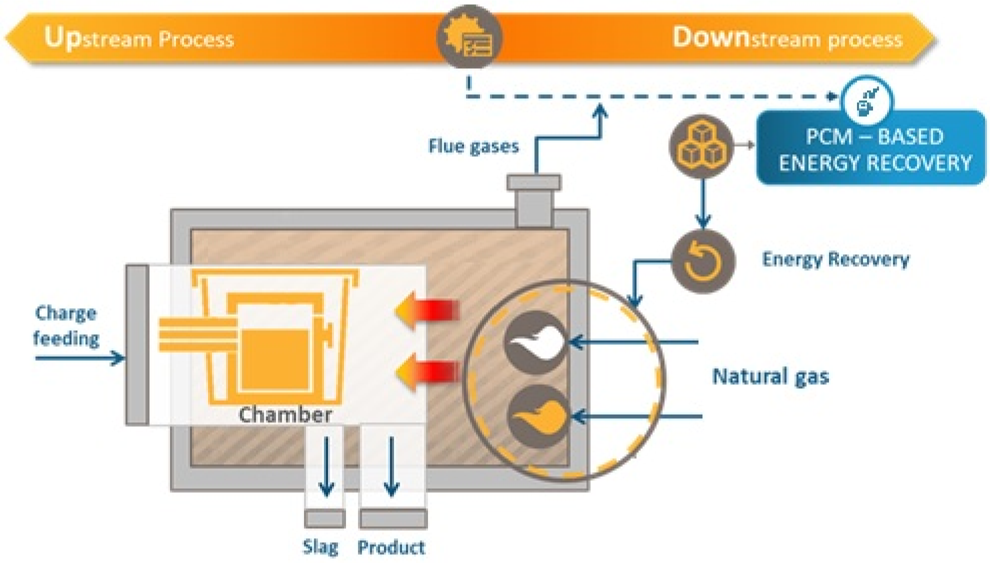

Figure 9. Diagram of PCM-TES integration in an industrial heating system.

This increase would allow overcoming the technological limitations to recover heat above the temperature that is currently reached using conventional systems. In addition, it is important to highlight the beneficial consequences of the energy, environmental and economic savings that come with increasing the overall efficiency of the system.

1.5.2 Specific objectives

- Investigation of the potential use of PCM at high temperature to recover energy from industrial furnaces and hurdle the implications in waste heat recovery characterised by high variability of flows and temperatures – Chapter 2 and 3.
- Design, at conceptual level, of the best configuration of PCM-TES solution by adapting the storage system to the end-user facilities and the potential heat sources – Chapter 4.
- Definition of sizing specifications, geometrical configuration and main equipment of the PCM-TES, according to the process requirements for each specific sector – Chapter 4 and 5.
- Modelling the thermal performance of the PCM-TES solution (charge/discharge periods, temperature profiles, velocity fields) in order to select the most suitable construction materials (PCM, shell, tubes and insulation) – Chapter 5 and 6.
- Prototyping and development of technical documents, drawings and process specifications of the PCM-TES by establishing the specific operating conditions and equipment necessary to achieve the level of reliability, efficiency and safety required – Chapter 7.
- Integration of the innovative thermal energy recovery system based on PCM for industrial heating systems, overcoming the current lack of information of PCM-TES applications at industrial level, especially at high temperatures – Chapter 7.
- Establishing the prospective validation of the design and the methodology for modelling the PCM-TES industrial prototype – Chapter 8.
- Validation of a simplified in-house model in order to provide reliable results for practical application in the engineering and industry sectors – Chapter 8.
- Assessment of the technical and economic feasibility for PCM energy recovery solutions in an industrial environment – Chapter 9.
- Demonstration of replicability in other materials, processes and sectors proofing the flexibility and suitability of PCM-TES integration – Chapter 9.

1.5.3 Overall methodology

The diagram in Figure 10 describes the design thinking methodology stages [46]. It is an iterative process where each phase represents a step forward through a product roadmap and increases the score along the technology readiness level (TRL) scale.

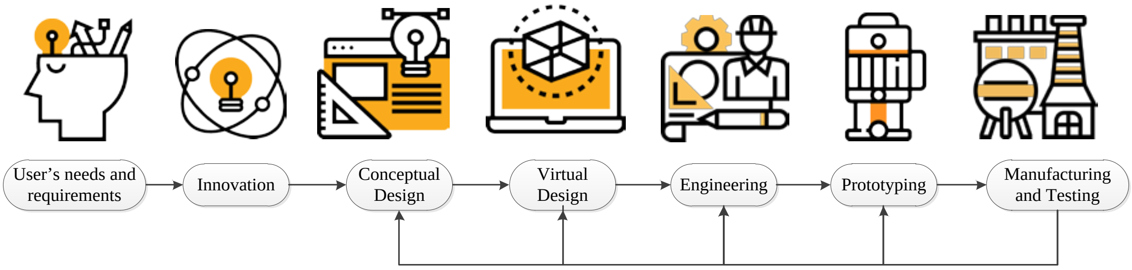

Figure 10. Overall methodology stages developed in the thesis, based on the design thinking process[8].

This methodology is established as the basis of the thesis chapters until the system prototyping. The first stage of the design thinking process allows gaining an empathetic understanding of the problem and gain real insight into users and their needs. To do so, the state-of-the-art review will be focused on the LHS technology based on PCM, as a potential solution for thermal energy storage and recovery in the EII sector. Additionally, specific research on PCM characterisation and their thermo-physical properties will be conducted. This process leads to stage two where the user's needs and requirements are stated and well defined, which allows setting the specifications of the innovative systems. It is necessary an assessment of the technical and economic feasibility, especially working with PCM at critically high temperatures.

After that, the thesis sets an owned developed methodology for conceptual design and integration alternatives of the innovative PCM-TES system. Two case studies in the ceramic and steel sectors are evaluated, the design engineering is set (sizing specifications, geometrical configuration) and the thermal performance for the PCM-TES solution (temperature profiles, charge and discharge processes, etc.) modelled using a numerical model approach suitable for practical applications at the industry. Virtual design technologies such as solid modelling and computer-aided simulations are an integral part of engineering practice [47]. The engineering will be based on the parameters defined by the conceptual and the performance expected from virtual design and operation. The engineering will set the final sizing, select the most suitable construction materials, costs, technical documents and drawings. This process allows implementing a comprehensive and functional physical prototype for the manufacturing and integration at plant level. In this way, the innovative system proposed is closer to finally reaching the market launch stage [48]. Finally, the PCM-TES system configuration is investigated in other cross-sectorial processes and applications by a simplified tool to demonstrate the replicability and feasibility.

1.6 Impacts

1.6.1 Impacts in the research and innovation field

In this respect, the thesis promotes an exponential advancement of the knowledge progress about PCM to overcome the challenges of implementing these materials at high temperatures, but also at medium and low ranges. This line of research allows widening and boosting the design and

[8] Icons designed by Flaticon from www.flaticon.com. Accessed in 2019

integration in EII of thermal storage and waste heat recovery systems based on PCM. The thesis development embraces a very valuable experience of participation in R&D activities. In addition, the thesis has been the basis for the publication of 6 scientific articles (with a total of 82 citations) in indexed peer-review international journals (Q1), 2 conference papers and 2 articles in national journals, along with 8 participations in prestigious conferences at European and national level. The article publications are gathered in Annexe 1.1 – Article publications.

ARTICLES

Patricia Royo, Víctor J Ferreira, Zafer Ure, Sam Gledhill, Ana M López-Sabirón, German Ferreira
Title**: Multiple-Criteria Decision Analysis and characterisation of phase change materials for waste heat recovery at high temperature for sustainable energy intensive industry**
Journal: Materials & Design (Peer Review Journal), *IF:6.289*
ISSN: 1359-43112019, Volume 186, 15. Date publication: January 2020

Patricia Royo, Luis Acevedo, Víctor J Ferreira, Tatiana García-Armingol, Ana M López-Sabirón, German Ferreira.
Title: **High-temperature PCM-based thermal energy storage for industrial furnaces installed in energy-intensive industries**.
Journal: Energy (Peer Review Journal), *IF:6.082*
ISSN: 1030-1040, Open Access Article Date: April 2019

Patricia Royo, Víctor J Ferreira, Ana M López-Sabirón, Tatiana García-Armingol, German Ferreira
Title: **Retrofitting strategies for improving the energy and environmental efficiency in industrial furnaces: a case study in the aluminium sector**
Journal: Renewable & Sustainable Energy Reviews (Peer Review Journal), *IF: 12.110*
ISSN: 1364-0321 ARTICLE. Date: 5 July 2017

Patricia Royo, Víctor J. Ferreira, Ana M. López-Sabirón, Germán Ferreira
Title**: Hybrid diagnosis to characterise the energy and environmental enhancement of photovoltaic modules using smart materials**
Journal: Energy (Peer Review Journal), *IF:6.082*
ISSN: 0360-5442. Volume 101, Pages 174-189. Date: 15 April 2016

Victor J Ferreira; Ana M López-Sabirón; **Patricia Royo**; Alfonso Aranda-Usón; German Ferreira
Title**: Integration of environmental indicators in the optimization of industrial energy management using smart materials**
Journal: Energy Conversion and Management - Peer Review Journal, *IF:* 8.208
ISSN: 0196-8904. Volume 104, Pages 67-77. Date: 01 November 2015

Ana M. López-Sabirón, **Patricia Royo**, Victor J. Ferreira, Alfonso Aranda-Usón, Germán Ferreira
Title**: Carbon footprint of a thermal energy storage system using phase change materials for industrial energy recovery to reduce the fossil fuel consumption**
Journal: Applied Energy - Peer Review Journal, *IF: 8.848*
ISSN: 0306-2619. Article - Volumen: 135, Pages 616-624, Date: 15 December 2014

Patricia Royo, Víctor J. Ferreira, Ana M. López-Sabirón, Germán Ferreira
Title**: Nueva generación de placas fotovoltaicas: evaluación técnica de la aplicación de materiales avanzados para optimizar su eficiencia**
Journal: Era Solar. Scientific article – Date: May-June 2015

Patricia Royo, Ana M. López-Sabirón, Víctor J. Ferreira, Germán Ferreira
Title**: Integración de materiales inteligentes en placas fotovoltaicas para aumentar la eficiencia ambiental y energética de los diseños convencionales**
Journal: Energías Renovables. Scientific article – Date: April 2015

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Patricia Royo, Luis Acevedo, A.Jorge Arnal-Mañas, Maryori Díaz-Ramirez, Víctor J Ferreira, Tatiana García-Armingol, German Ferreira, Ana M López-Sabirón
Title: **Novel heat recovery system for ceramic furnaces using high-temperature phase change materials and integration based on multicriteria analysis development.**
Oral communication and Conference Paper. Conference: 12th European Conference on Industrial Furnaces and Boilers – **INFUB 2020**; Porto, Portugal. Submitted and accepted - October 2020

Patricia Royo, Nele David, Maike Johnson, Ana M López-Sabirón, German Ferreira, Dan Bauer.
Title: **Experimental Validation Of A Hybrid Power-To-Heat Storage Based On High Temperature Phase Change Materials To Enhance Sector Coupling And Flexibility.**
Oral communication and Conference Paper. Conference: International Renewable Energy Storage– **IRES 2020**; Düsseldorf, Germany (Online conference). 25/05/2020-26/05/2020

Patricia Royo, Luis Acevedo, A Jorge Arnal-Mañas, Maryori Díaz-Ramirez, Víctor J Ferreira, Tatiana García-Armingol, German Ferreira, Ana M López-Sabirón*presenter
Title: **Advanced retrofitting solution for furnaces and processes as a key path towards creating eco-efficient and competitive energy intensive industries.**
Oral communication. Conference: Advances in Energy Systems and Environmental Engineering **ASEE 2019 -** Worclaw, Poland. 09/06/2019-12/06/2019

Patricia Royo, Luis Acevedo, Víctor J Ferreira, Tatiana García-Armingol, Ana M López-Sabirón, German Ferreira.
Title: **Thermal performance investigation on latent heat thermal storage for waste heat recovery from a high temperature gas flow in energy-intensive industries.**
Oral communication. Conference: **IAPE 2019 -** International Conference on Innovative Applied Energy; Oxford, United Kingdom. 14/03/2019-17/03/2018

Patricia Royo, Victor J. Ferreira, Ana M. López-Sabirón, Germán Ferreira
Title: **Novel advanced thermal energy storage system for smarter use of secondary feedstock of existing furnaces in energy-intensive industries, including industry 4.0 perspective**
Oral communication Conference: **AEMC-2018** – Advanced Energy Materials Conference Stockholm, Sweden. 25/03/2018-28/03/2018

Patricia Royo, Luis Acevedo, Víctor J. Ferreira, Tatiana García-Armingol, Ana M. López-Sabirón, Germán Ferreira
Title: **Computer-aided design for high temperature PCM-based TES working with combustion exhaust gas flow of industrial furnaces installed in the energy intensive industries,** Oral communication-Archival;
Conference: International Conference Contemporary Problems of Thermal Engineering - **CPOTE 2018;** Gliwice – Poland. 18/09/2018-21/09/2018

Patricia Royo, Victor J. Ferreira, Ana M. López-Sabirón, Tatiana García-Armingol, Germán Ferreira
Title: **Retrofitting strategies for improving the energy and environmental efficiency in furnaces** Oral communication-Archival
Conference: 11th Conference on Sustainable Development of Energy, Water and Environment Systems **SDEWES 2016;** Lisbon, Portugal. 04/09/2016-09/09/2016

Patricia Royo, Victor J. Ferreira, Ana M. López-Sabirón, Germán Ferreira
Title: **Innovative solution to prevent the material degradation in photovoltaic modules: technical and environmental implications**: Oral communication
Conference: **ACE-x 2015 -** 9th International Conference on Advanced Computational Engineering and Experimenting in: Munich, Germany. 29/06/2015-02/07/2015

1.6.2 Impacts of technological advance in the industrial sector

The results coming from this document not only promotes new technological solutions in terms of research and innovation, but also sets a basis for the deployment and advancement of solutions at industrial scale. This is an important step to accomplish the full innovation chain of innovation in industrial applications. In this thesis, the original design of the WHR system based on PCM starts from conceptual development, through design and basic engineering, and finally, to its integration into an industrial plant under real operating conditions (TRL 7).

Thus, this thesis contributes to seeking strategies to update the mainly old-aged industrial processes, and also initiating a path to ensure successful integration, in case of new equipment implementation. With this level of readiness and demonstration comprises a strategy to narrow the gap of the well-known Valley of Death (Figure 11), by achieving:

(i) incremental improvements to existing technology and materials, especially at high temperatures, which are currently at TRL 4-5 (technology validated in lab and in a relevant environment in the case of key enabling technologies)

(ii) the integration of innovative TES technically reliable and with the potential to become commercially ready at industrial scale in the medium term TRL 9 (actual system proven through successful mission operations).

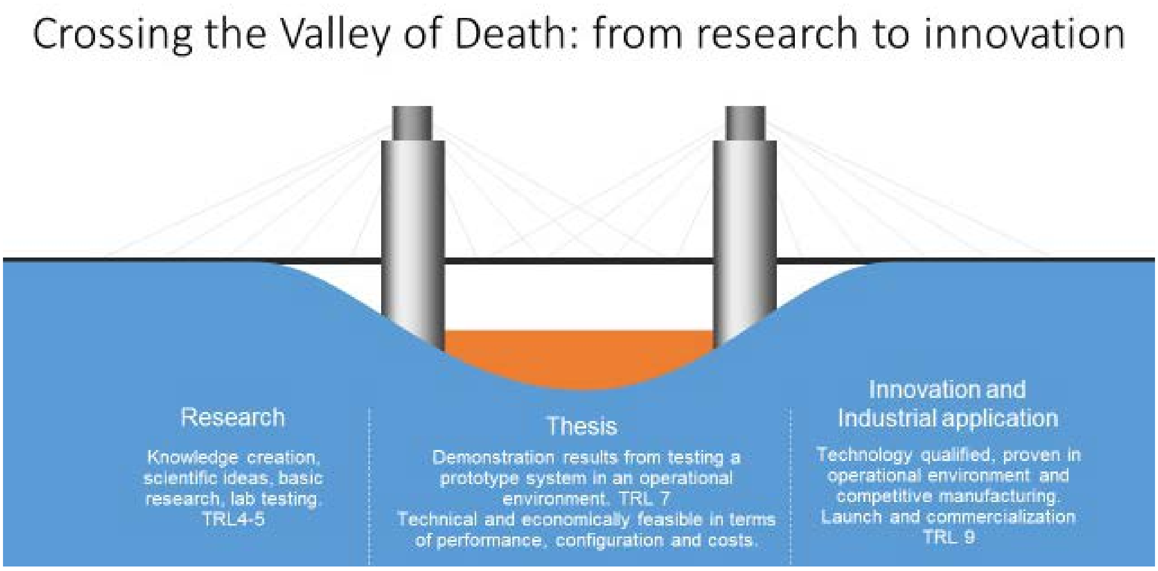


Figure 11. Thesis contribution in bridging the gap of Valley of Death.

In short, the solution developed during the thesis will be of great impact for a model industry where the PCM-TES would be integrated, mainly in three pillars that are detailed below:

- Increase in energy efficiency: +10% efficiency
- Reduction of energy consumption: 850 MWh/year
- GHG emissions avoided: 200 tons CO_2 eq./year
- Economic benefits: 58 k€ saved/year

In this sense, more than 5000 potential end-users (European industries) with a total consumption of 130 TWh/year of natural gas [26] have been previously detected, thanks to the broad flexibility and replicability offered by these systems. Assuming that 15% of potential industries will implement the project solution in 20 years, up to 2 TWh/year of natural gas could be saved, with the consequent effect of reducing 0.5 million tons of CO_2 equivalent.

Finally, other indirect impacts are explained in more detail hereafter**:**

- Promote eco-innovation and a strong commitment to sustainable development in global markets reducing the energy dependence on fossil fuels by the introduction of energy-saving technology.

- Enlarge the replication potential of PCM-TES and ensure that cross-sectorial approach, adapting the designs depending on the specific requirement of the plant, what increases its replicability in many EII sectors.

- Starting for the consolidation and validation via innovative technology based on new smart materials integrated at very high temperatures to improve the performance of the EII operations at process, plant and multi-plant level.

- Increase the market competitiveness and employability by means of opening new technologies aligned with the last technological trends and roadmaps to overcome future energy challenges.

«If I have seen further, it is because I have stood on the shoulders of giants»

Isaac Newton

2 - LITERATURE REVIEW

2.1 Thermal energy storage technology

2.1.1 Description and motivation for integration

There are a large number of processes in which thermal energy is lost every day, especially those processes running at low and medium temperatures [49]. In addition to the reduction in the amount of excess energy released by production processes, several options are available for the use of industrial excess energy, including heat harvesting, heat storage, heat utilization and heat conversion technologies [50]. Different technologies, ranging from storage solutions to heat pumps and converters, have been developed in order to make this possible. The utilisation of currently unused process waste heat has an immense potential to save primary energy and to decrease the environmental impact. This energy is commonly called waste heat, and its optimal use represents a significant opportunity to establish advanced TES technologies [51]. TES systems store waste heat and then release it in combination with power generation, building thermal comfort and many other niche industrial applications.

A TES system consists of three parts, the storage medium, heat transfer mechanism and container system [52]. The thermal storage works on a cyclic process, which involves a charging phase, then energy storage, and finally the discharging from the medium. The purpose of the energy transfer mechanism is to supply or extract heat from the storage medium. The containment holds the storage medium as well as the energy transfer equipment and insulates the system from the surroundings. Some systems are considered as active, where the heat transfer fluid will also serve as a storage medium; while in passive systems, the heat transfer fluid passes through a different storage medium where the thermal energy is stored. Thermal energy (i.e. heat and cold) can be stored using three methods, as sensible heat in heat storage medium, as latent heat associated with phase changing or as thermo-chemical energy associated with chemical reactions. These three technologies are depicted in Figure 12, according to its heat storage capacity [53].

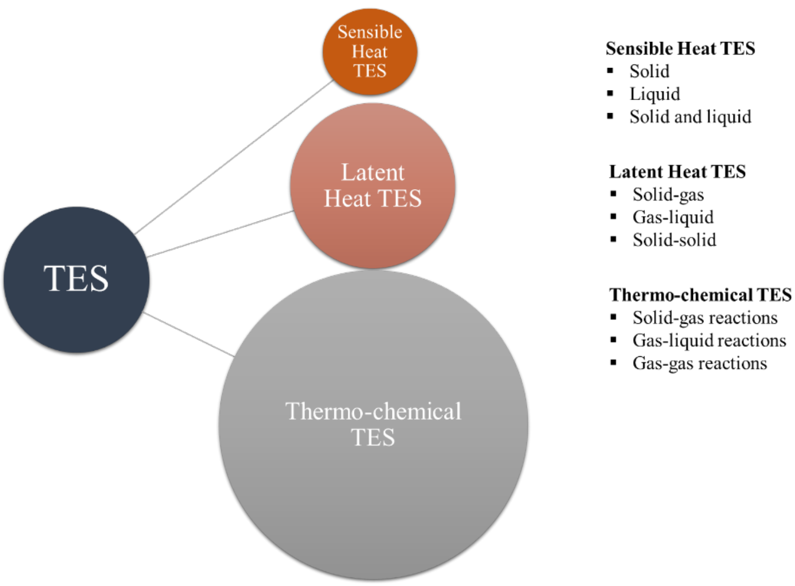


Figure 12. Diagram of TES methods and the heat storage capacity sizing-ratio.

Firstly, the use of hot water tanks is a well-known technology for sensible heat TES, which serve the purpose of energy saving in water heating systems based on solar energy and in co-generation energy supply systems. Secondly, LHS is a promising alternative that can reduce the size (3-4 times more storage capacity), operational failures, environmental impact and both manufacturing and operating costs of several industrial systems that cannot manage the waste heat generated during their operation. In essence, the combination of heat exchangers with LHS applications results in an attractive way to store a large amount of waste heat generated during discontinuous operation and to dissipate the heat during steady state operations [54]. Finally, a higher energy density TES system can be achieved using chemical reactions (up to 10 times comparing to sensible heat storage), such as adsorption (i.e. adhesion of a substance to the surface of another solid or liquid), which can be used to store heat and cold, as well as to control humidity. The most appropriate TES technology should be chosen according to the adequacy of its safe performance, the technical requirements of the application, the economic feasibility and the technological level of maturity.

2.1.2 Classification of thermal storage technology

The materials used for thermal energy storage are divided into three categories depending on the storage mechanisms used [55]: either in the form of sensible heat (Figure 13.a), latent heat of fusion or vaporisation (Figure 13.a), or in the form of reversible thermo-chemical reactions (Figure 13.b).

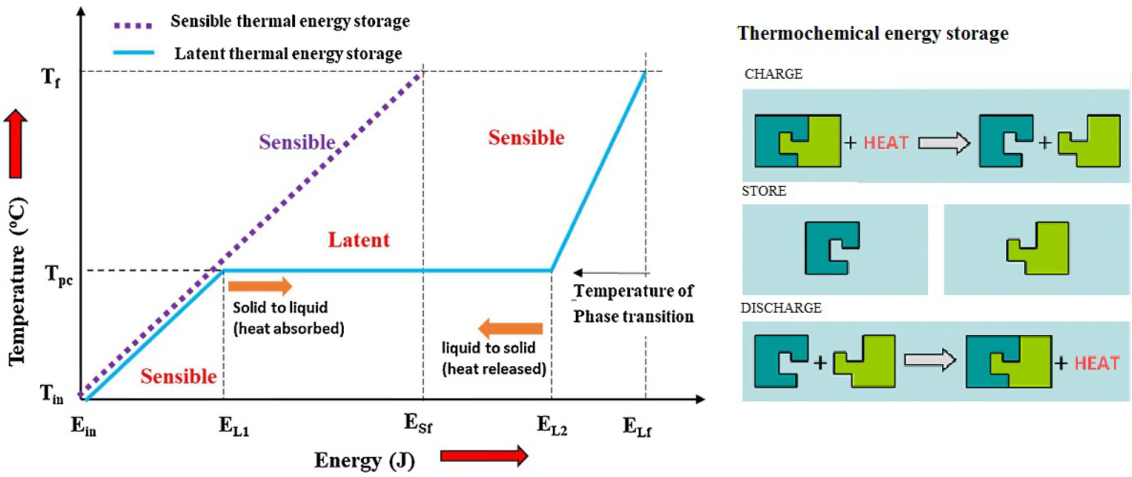


Figure 13. Schematic diagrams for TES working principles: sensible vs. latent heat (left) and thermo-chemical (right) [56, 57].

- **Sensible heat systems (SHS)** are based on the energy absorbed by a body that raises its temperature without affecting its molecular structure and therefore without affecting its state. The heat stored (Q_s) is directly proportional to the difference in temperatures (T_{ini}, T_{fin}) it is subjected to (from initial to final) and mass of the body or substance (m) and it is defined by Eq. (1). This proportionality constant is the specific heat (c_p), and it depends on the specific storage medium. Sensible heat is the most developed and economical technology; however, it has the lowest storage capacity and significantly increases the size of the system. Some of the most widely used systems are based on rock, sandstone, metals, brick, soil, molten salts and concrete [58].

$$Q = m\, c_p(T_{fin} - T_{ini}) \tag{1}$$

- **Latent heat storage (LHS)** is based on the latent heat of fusion of PCMs, which is the energy required by a body to change its phase by modifying its molecular structure. While PCM is changing phase, it is considered a quasi-isothermal process, since the temperature remains practically constant. Latent heat is directly proportional to the mass and latent heat of fusion. Unlike storage based on sensible heat, latent heat can offer higher energy storage density (200 kJ/kg), which is more than 3-4 times higher than the sensible heat, so it significantly increases the thermal storage capacity and reduces the volume of the system. However, it has low thermal conductivity values (0.2-1 W/(m·K)) [59], therefore heat transfer enhancement techniques are recommended to be adopted in order to assure a higher thermal efficiency. Although these systems are commercially available, they still present a high technical risk. In this case, the storage capacity is given by the mass of the storage material (m), the sensible heat capacity, before and after the phase-change transition temperature of the PCM (T_{pc}); additionally to the heat latent determined by and the enthalpy of fusion or vaporisation (ΔH_{latent}), according to Eq. (2).

$$Q = m\, c_p\, (T_{pc} - T_{ini}) + \Delta H_{latent} + m\, c_p\, (T_{fin} - T_{pc}) \qquad (2)$$

- **Thermo-chemical materials (TCM)** can absorb and release a large amount of thermal energy during endothermal/exothermal reactions [59]. The energy is stored after a breaking or dissociation reaction of chemical bonds at the molecular level which releases energy and then recovered in a reversible chemical reaction [60]. A suitable reaction system for TES is generally challenging since materials must be reversible chemical reactions during absorbing/releasing, involving a large amount of heat (reaction enthalpy of change around 1000 kJ/kg [58]). Examples of potential materials for chemical heat storage are metal hydrides, ammonia, calcium and sodium carbonates, aluminium ore, alumina, zeolite and silica gel. This type hold the greatest storage capacity; approximately 8–10 times higher storage density than sensible heat systems and 2 times higher than latent heat [58]. They can store thermal energy for a long duration with low heat losses, appropriate for seasonal storage [56]. Nevertheless, the processes are restricted by their novelty because they have not been extensively researched, are hindered by complicated reactors, and have shown certain instability and weak reversibility in the long term. In this case, the heat stored depends on the endothermic reaction enthalpy for a specific amount (ΔH_r) and the extent of conversion or fraction reacted (a_m), as it is presented in Eq. (3).

$$Q = a_m \Delta H_r \qquad (3)$$

2.1.3 Technical, environmental performance and cost-effectiveness

Depending on the type of storage, several requirements must be considered to ensure optimal storage. Among these main requirements, the objective is to seek a compromise of high energy density in the storage material, mechanical and chemical stability, material compatibility, reversibility in the charge and discharge cycles, low thermal losses, cost-efficiency and minimum environmental impact [61]. For example, since the energy density is one of the most important parameters Figure 14 represents this parameter for the TES medium as a function of the operating temperature [58].

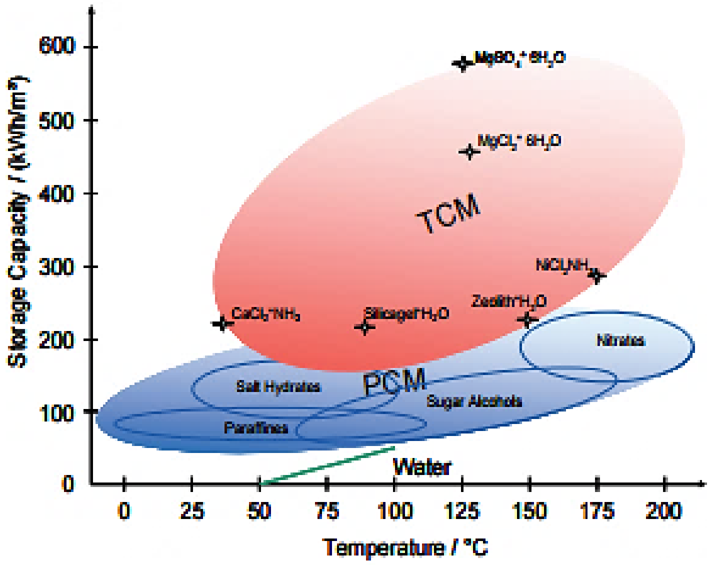


Figure 14. TES comparison in function of energy density and operating temperature [62].

Conventional sensible storage systems report the lowest storage density, which reduces its heat storage capacity and is restricted to large volumes. Besides, the use sensible heat to increase the temperature of water tanks enlarges the temperature gradient when storing/releasing thermal energy instead of working at a nearly constant operating temperature. Unlike sensible heat storage, PCMs, as latent heat storage, can release and absorb great quantities of heat and the temperature is approximately constant during phase change, due to the isothermal phase change mechanism [63]. Usually, the solid–liquid phase change is used. The PCMs are also appropriate materials, especially in the low and medium temperature range, where are very much developed. Finally, the chemical and sorption-based reactions achieved both the highest density and temperatures. However, the level of maturity of this method still presents a lot of challenges to overcome [55].

Thus, when selecting a storage system, it is important to review the advantages and disadvantages offered by each type [64-67], which can be summarised as follows in Table 2:

Table 2. Summary of the main properties of different TES technologies.

TES type	Sensible	Latent	Chemical
Storage Medium	Water, gravel, pebble, soil	Organics, inorganics, eutectics	Metal chlorides, metal hydrides, metal oxides…
Type	Water-based system Rock or ground-based	Active storage Passive storage	Thermal sorption (adsorption, absorption) Chemical reaction
Energy density (kWh/m^3)	Small ~50	Medium ~100	High ~500
Storage period	Limited	Limited	Theoretically unlimited
Operation temperature (ºC)	Up to 450	Up to 900	Up to 400
Technology complexity	Simple	Medium	Complex
Efficiency (%)	50-90	75-90	75-100
Cost (€/kWh)	0.1	10-70	10-100

Advantages	Environmentally friendly cheap material	Higher energy density than sensible heat storage	Highest energy density
	Relatively simple system, easy to control	Provide thermal energy at constant temperature	Compact systems
	Reliable		Negligible heat losses
Disadvantages	Low energy density, large volumes	Lack of thermal stability	Poor heat and mass transfer under high density condition
	Self-discharge and heat losses problem	Crystallization and corrosion issues	Uncertain cyclability
	High cost of site construction	Low thermal conductivity	High cost of storage material
	Geological requirements	High cost of storage material	Lowest level of maturity
Durability (years)	20 years	5 years	2 years
Maturity status	Large-scale industrial demonstration plants	Material characterization, laboratory-scale prototypes and a few pilot plant demonstrators	Material characterization, laboratory-scale prototypes
Commercial viability	Commercially available	Some materials are commercially available	In research phase, not commercially available
Future Work	Optimisation of control to advance solar fraction and reduce power consumption	Screening for better suited PCM materials with higher heat of fusion	Optimisation of particle size and reaction bed structure to get constant heat output
	Optimisation of storage temperature to reduce heat losses	Optimal study on store process and concept	Optimisation of temperature level during charging and discharging
	Simulation of ground/soil-based system with the consideration of affecting factors (e.g. underground water flow)	Screening for more suitable and economical materials	
		Further thermodynamic and kinetic study, noble reaction cycle	Further thermodynamic and kinetic study, noble reaction cycle
Transport	Short	Medium	Theoretically unlimited

As a conclusion, sensible heat storage based on the use of water, rock or ground, is a reliable and cost-efficient alternative for long-term/seasonal storage. The simplicity of water-based storage is very suitable for residential applications, although the temperature range of operation is limited just for some specific industrial cases. Furthermore, sensible heat storage systems are often integrated with heat pumps to upgrade the temperature level. However, it has greater risks of heat losses at high temperatures and it presents restrictions at storing large amounts of heat with the same mass of material [66].

In this sense, thermo-chemical storage represents the best alternative due to the high energy density of the storage medium material (180-540 kWh/m^3) with negligible heat losses [68]. This kind of storage system can be more compact than other alternatives, and the selection of working pairs allows adapting the TES in accordance with the thermodynamic requirements and operating conditions. The operating temperature for this storage technology can be done at ambient temperature [66], but in general the middle operating range is between 200 and 400ºC [69]. The sizing of the sorbent and the design of the bed structure are critical steps to guarantee an acceptable and compact system ensuring a constant output flow rate. In addition, other restrictions are the high investment costs and the poor heat and mass transfer at high density conditions. The thermo-chemical feasibility has been demonstrated in some chemical heat pumps and both long and short-term storage systems [69], nevertheless there is still a strong need for further implementation at large-scale [67].

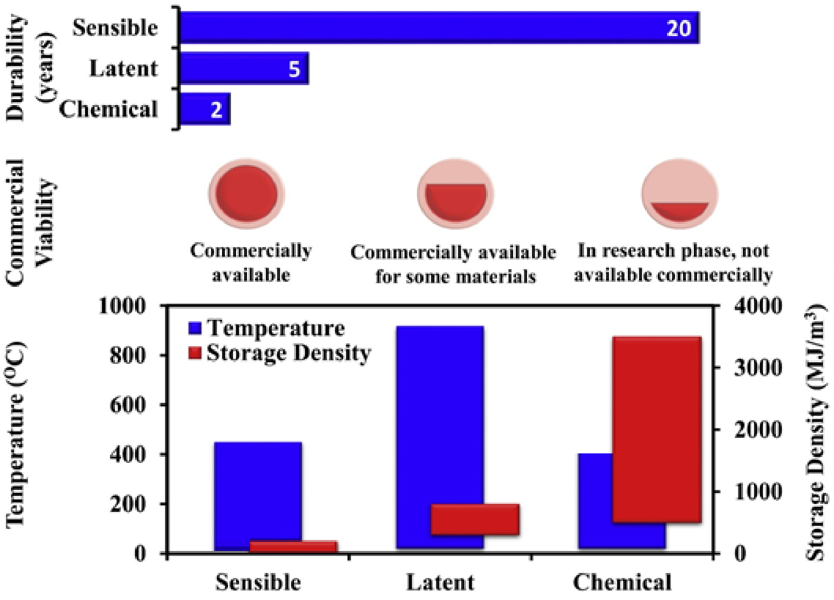


Figure 15. Comparison of operation, viability and durability for TES technologies [68].

In light of the above, LHS represents an alternative that meets the compromise between still an innovative strategy but with a promising performance (as illustrated in Figure 15) in comparison with SHS and TCM. A PCM-TES, as latent heat storage, has a higher energy density than sensible storage and features the ability to provide the stored energy at a nearly constant temperature during the phase changing. Most of the challenges of these materials arise from the material stability, segregation, corrosion and low thermal conductivity [70, 71]. In order to solve this, many studies are focused on the encapsulation of these materials at different scales [72] and material characterization. At present, there are a wide number of lab-scale prototypes and pilots. However, experiments and implementation under real operational conditions are an unavoidable priority to achieve a large-scale practical use and a future commercialisation. This shortage is even more pronounced at high temperature levels where the thermal stability, compatibility and corrosion problems are highlighted [73].

Although the initial objective of these systems are energy savings and increase the efficiency, the overall environmental assessment of this TES technology is very important for granting the environmental sustainability of these systems. To this end, the Life Cycle Assessment (LCA) methodology was used by several researchers as a tool to estimate the environmental impact of TES systems with a specific PCM and specific applications. For instance, a solar thermal collector with integrated water storage [74], molten salts for concentrated solar power plants [75], salt hydrates for construction materials [76] or even considering other types of energy storage systems such as battery energy storage, pumped hydro storage or compressed air energy storage [77]. In the different scenarios for PCM-TES studied by, the highest environmental benefits were achieved by LiOH/KOH for most options of the application scenarios [78]. As a general perspective, these authors suggested that incorporating PCMs substantially reduce the overall environmental impact under the experimental or theoretical conditions studied.

Regarding the cost estimation for TES systems should consider the storage material, technical equipment for charging and discharging, and operation costs. In general, sensible heat TES are rather inexpensive as they consist basically of a tank for the storage medium and the equipment to charge/discharge. However, the container of the storage material requires effective thermal insulation; otherwise, it would be rapidly discharged. Most seasonal TES systems consist of approximately 10000 m^3 water container, which allows an energy storage 70-90 kWh/m^3 and whose investment costs ranges from 0.5 to 3.0 €/kWh [62] for low temperatures; while for small residential use this cost goes up to 40 €/kWh [79]. In case of sensible heat based on underground TES, the costs go up to 10 €/kWh [62].

In general, the cost of a PCM system ranges between 0.1 and 10 €/kWh in case of low and medium temperatures; while it is increased between 20 and 70 €/kWh for higher temperatures [64]. Nevertheless, the difference between the PCM as storage material cost contribution and the complete TES system is even higher for PCM installations. As an example, the costs of a Glauber salt (calcium-chloride material), which is inexpensive (0.10−0.20 €/kg), it is increased up to 70 €/kWh by the cost of container, heat exchanger and other surrounding components. The price of the bulk PCM for TES application covers a wide range, reaching up to 300 €/kg [80]; while most organic PCM are commercialised around 1.5−5 €/kg [81]. Among the inorganic compounds, there is a great difference between molten salts and metal alloys. The latter presents the highest prices while the hydrated salts usually range from 1 to 4 €/kg [82]. Very few of them are more expensive, such as LiCl with a cost of around 8 €/kg [83]. When there is a need of encapsulating or stabilised the bulk material the price increases. For example, the cost of a complete plaster board is 17 €/kg and paraffin pellets encapsulated in HDPE with an enthalpy of around 100 kJ/kg would approximately cost 6-8 €/kg [62]. Finally, the smaller scale of encapsulation the higher prices are reported. The system cost using microencapsulated PCMs, which avoid the use of heat exchange surfaces, can be even two or three times higher.

Materials for thermo-chemical storage are also expensive and complex to prepare (e.g. in form of pellets or supported layers). Moreover, in most cases they need enhanced heat and mass transfer technologies to achieve the expected performance in terms of storage capacity and power, and the cost of the equipment is much higher than the cost for the storage material (for instance, limestone is a very cheap material, 0.05 €/kg, [62]). In general, this kind of TES requires an investment cost in the range of 10-45 €/kWh with a storage capacity of 120-150 kWh/ton [64].

On the one hand, sensible hat storage is more cost-efficient in long-term and seasonal applications where the volume is not a restriction. On the other hand, PCM and thermo-chemical systems, which generally are more expensive, are economically more suitable for applications with at least 1000 cycles per year; then, the viable investment cost can be even higher than 250 €/kWh [62].

In conclusion, each storage application needs a specific TES design to meet the operational conditions and end-user requirements. The current research deals with designs for a proper process integration, materials (i.e. characterization of storage media for different temperature ranges), containers that ensure material compatibility and thermal insulation development [62]. In short, more efforts need to be made in order to boost PCM-based latent heat storage technology, and this is addressed in the thesis. Especially, more complex systems (such as PCM-TES) require R&D efforts to deepen the understanding of system integration at industrial scale, the thermal performance and the influence of key process parameters.

2.2 TES based on PCM

2.2.1 PCM definition

Among the different TES presented in the section above, this thesis is focused on the use of latent heat systems based on PCMs as energy recovery and storage systems. These materials allow the energy to be stored and released in the form of latent heat of fusion at an almost constant temperature. A PCM is defined as a substance or compound capable of storing and releasing latent heat, maintaining a constant temperature during heat absorption or dissipation process. There are three different types of phase change of the material: solid-liquid, solid-solid and liquid-vapour.

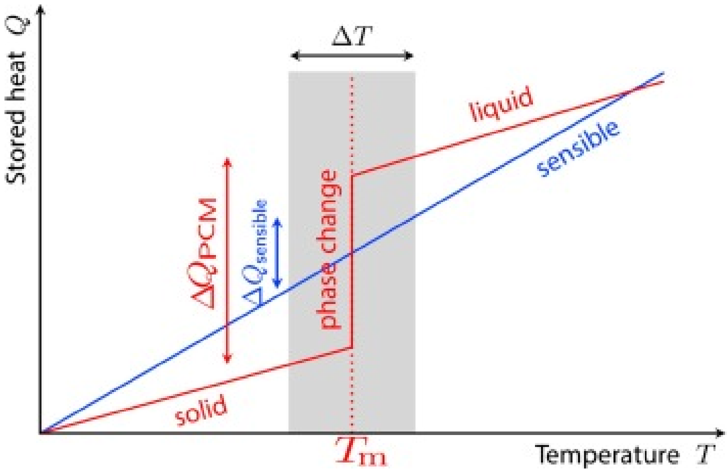


Figure 16. Diagram of the stored heat variation of a PCM with increasing temperature [84].

The heat latent transfer of a material is equal to its variation of enthalpy (ΔH) between the two different phases (usually, liquid and solid). Normally the fusion temperature of the PCM is selected in the operation range of the process that is meant to be managed. If this temperature meets the phase change transition, the ΔQ_{pcm} is much higher than the achieved with a sensible heat system $\Delta Q_{sensible}$, as it can be seen in Figure 16. Hence, PCM systems are a potential solution to store energy in a relatively small volume.

The different melting temperatures of PCM along with the variety of both collector and storage configuration originate a great versatility of integration. The working principle is to increase the PCM temperature when heat is available, in order to achieve a continuous melting, turning the PCM into liquid. During the phase change, the latent heat of fusion allows the storage of a higher amount of heat. Then, a HTF that can be air or water flows through the PCM-TES, which releases the heat as to the solidification process. According to the research presented by Wang et al. [85] and Lopez-Sabiron et al. [86], the benefits reported to this kind of system are mainly:

- Energy storage density increase: 39%
- Overall system efficiency: 42-77%
- Exergy efficiency increase: 6-16%
- Annual savings on space heating and hot water: 88%
- Annual savings on the heating bill: 61.5%
- Service period of supply water: 25% longer
- Decrease in the total lifecycle cost with the increase of HTF flow rate

2.2.2 PCM classification

Based on the chemical composition, PCMs are classified into three main types: organic, inorganic and eutectic [87], depending on the material nature. Organic materials are normally more suitable for operating temperatures below 100ºC; otherwise, inorganic materials (salts and metals) may fulfil higher temperature requirements (over 1000ºC [88]). Thus, this group and its eutectic mixed variety offer adequacy for developing applications in the EII sector [78]. The most relevant sub-groups are defined in Figure 17 and the characteristics are described in the following sections.

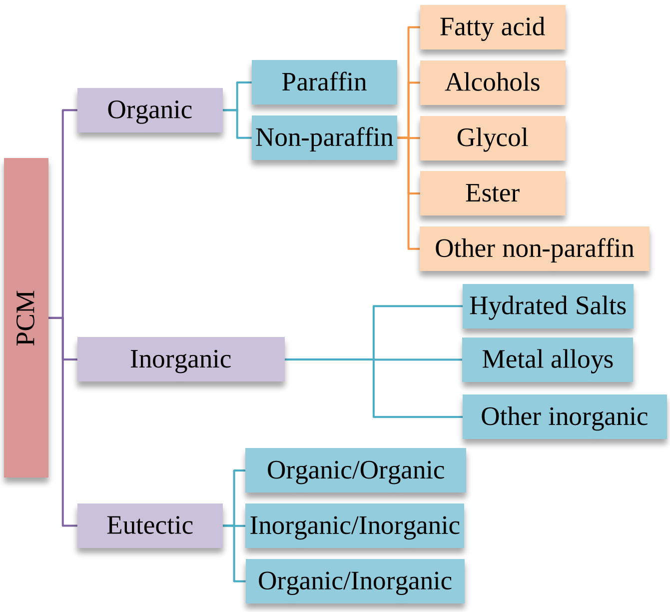


Figure 17. Schematic classification of PCMs by chemical composition.

- **Organic**

Organic materials are divided into paraffinic and non-paraffinic compounds. They can self-nucleate without subcooling or segregation during various cycles and are non-toxic, non-corrosive and recyclable [89]. They have high latent heat of fusion (150-200 kJ/kg) but low thermal conductivity (around 0.2 W/m·K) [90], leading to low charging and discharging rates [91]. Paraffin waxes consist of a mixture of mostly straight chain n-alkenes, whose crystallization release large amounts of latent heat. Both heat storage capacity and fusion temperature increase with the chain length. Paraffins are safe, reliable, less expensive, non-corrosive and stable. The other main sub-group is non-paraffin organic PCMs. Among other, alcohols, fatty acids, glycols and esters are included in this category. These kinds of compounds exhibit high heat of fusion, low thermal conductivity, low flash points and instability at high temperatures because they are flammable. Despite that, they are the most numerous, present a wide variety of properties and are more readily available for many uses [55]. The application of organic materials is very common, especially low temperature fields, such as heating and domestic hot water systems, cooling of buildings and solar energy accumulator [92].

- **Inorganic**

Inorganic PCMs do not appreciably suffer from subcooling and their melting enthalpies do not degrade with cycling. The two main types are hydrated salts and metal alloys. Salt hydrates have been extensively studied in heat storage applications because of their positive characteristics and are known for their high storage density (175-225 kJ/kg), higher thermal conductivity than organics (0.7-1 W/m·K) [93], abundant availability and economic cost [94]. The volume of these salts changes greatly when changing phase during subcooling and incongruent segregation [95], which can be tackled by adding thickening agents, by mechanical stirring, by encapsulating the PCM to reduce separation, etc. In the other subgroup, the majority of materials are metals and their alloys. Metals have excellent thermal conductivity (over 100 W/m·K) and high melting points, conversely, they are expensive and heavy compared with other PCMs [55]. Besides, metal materials oxidize, and their application to PCMs can degenerate and reduce the thermal conductivity in the long term [92].

- **Eutectic**

Eutectic materials are mixtures of two or more organic and/or inorganic compounds, with similar (congruent) melting and freezing points, thus taking advantage of the combined properties. These compounds have precise melting points similar to that of pure substances, and their volume density is slightly above that of organic compounds [96]. However, they have low latent and specific heat capacities. The weight percentage of each material can be adjusted to obtain variations in the melting point of the resulting mixture [97]. They represent a very promising group but still under research. Their use in the field is recent and less diffused than the other groups and controversial information has been presented on their thermo-physical properties.

In order to identify the possible alternatives to implement a PCM system, it is necessary to develop an updated inventory of possible materials for different operating conditions to gather and organise the different types of materials by typology (organics, inorganics and eutectics). Based on the literature above, PCM inventory tables in function of the classification were developed and they are gathered in Annexe 2.1.

2.2.3 Stability and lifetime

Despite the advantages offered by these materials, considerable challenges must still be overcome, such as corrosion, reactivity, compatibility, structural resistance and safety issues. The instability of long-term PCM is considered due to two factors: the low stability of the physical and thermal properties of the materials and/or the corrosion between the PCM and the container [43, 98]. It is very important to carry out the cycling stability tests in order to ensure the long-term performance of a storage unit [70].

On the one hand, a PCM is reliable if it is thermally, chemically and physically stable after several repeated thermal cycles. However, PCMs may degrade over time and lose its thermo-physical properties, such as phase-change temperature variation, enthalpy of phase change, decrease in PCM density or loss of PCM mass or water. Even more, degradation is more crucial at high temperatures due to considerably higher loss of mass. Besides, other problems like subcooling, phase separation and loss of chemical properties must be also considered. The most widely used techniques for PCM characterisation are differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) [99-103], which allows a study of the status along cycles. Most of the references are based on experiments carried out in laboratories of materials subjected to accelerated thermal cycles, to determine the material maintains its thermal properties unchanged if in a specific number of cycles (50, 100, 1000 or even 5000 cycles).

Some authors, like Farid et al. [94] made an analysis of the properties of PCMs and their possible applications and the projection of existing problems in some PCM, such as phase separation, subcooling and the degradation speed of thermal properties in the long term. Rathod and Banerjee [71] showed in a review about thermal stability of PCMs used as latent heat TES systems, all thermal cycling test results that have been carried out concerning all types of PCM For example, some data was provided by Laing et al. [104], who analysed the charge and discharge cycles and observed that after 250 thermal cycles retained its functionality. Shukla et al. [105] performed a thermal cycling test of erythritol, which proofed to be a promising PCM for high temperature TES, as only showed gradual degradation after 500 thermal cycles. Kaizawa et al. [106] also presented erythritol results under repeated cycles with a large capacity of 344 kJ/kg at melting point of 117ºC, a high decomposition point and an excellent stability. Moreover, the study developed by Palomo et al. [107] revealed a high thermal stability for the binary mixture system LiOH/KOH. Additionally, based on the test performed by Michels and Pitz-Paal [108] to some compounds such as $NaNO_3$, KNO_3/KCl and KNO_3, an average charge and discharge time for the PCM of 6 hours per cycle and 4000 hours of lifetime were assumed by Steinmann et al. [109]. Nevertheless, in agreement with Kenisarin [70, 71, 88, 110-112] among others, there is not a sufficient amount of information about the behaviour of PCMs undergoing repeated cycles of fusion and solidification in realistic scenarios, and even less at high temperatures.

On the other hand, the PCM-container system's compatibility has limited the widespread use of PCM as LHS systems. Sarı and Kaygusuz [113] studied the corrosion resistance of some container material (stainless steel, carbon steel, aluminium and copper) tested for long exposure periods. Feilchenfeld et al. [114] used a scanning electron microscope after 500 cycles to study the compatibility of acetanilide as PCM with containers of materials such as aluminium (almost no corrosion) and stainless steel (very strong corrosion). All the tested PCM by Moreno et al. [115] presented very low corrosion rate when working with stainless steel, so the salt hydrated whose melting point is 50ºC, are recommended to be contained by this alloy. In the study of Ferrer et al. [116], stainless steel 304, stainless steel 316, and copper showed great resistance to inorganic salt's corrosive effects. So, its suitability to be used as this inorganic salt container is recommended, although it should be further tested at high temperatures. On the other hand, aluminium and carbon steel showed surface degradation, colouration and bubbling (Figure 18).

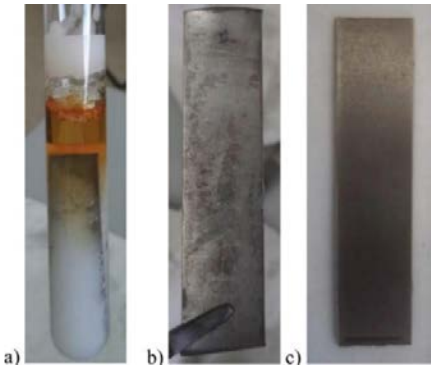


Figure 18. a) Carbon steel specimen immersed in an inorganic salt after 12 weeks. b) The same carbon steel specimen once cleaned. c) Non-tested carbon steel specimen [116].

2.2.4 Encapsulation

It is recommendable to encapsulate the PCMs for technical use in order to avoid most of the previously exposed problems related to stability, segregation and degradation. Containment of PCMs helps to keep the material in liquid and solid phases to prevent its possible variation in chemical composition by interaction with its surroundings, to increase its compatibility with other materials, to increase its handiness, and to provide a suitable heat transfer surface. Encapsulation is a key issue for the implementation of these technologies and must be designed to avoid leakage and corrosion. The encapsulation concept consists of enclosing the PCM core material by means of coating material, shell or embedded, similarly as illustrated in Figure 19 [68]. Furthermore, this technique provides more advantages for LHS: enhancement of the heat transfer area with PCM capsules; capsule walls act as barriers against harmful environmental reactions; the structural stability is enhanced and the material is easy to handle as a solid element [117].

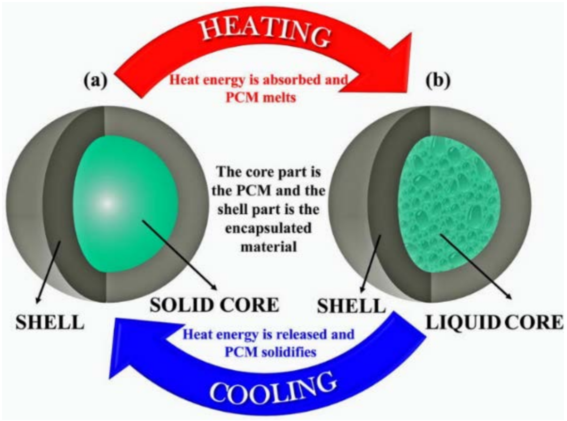


Figure 19. Diagram of the encapsulation concept [68].

Most encapsulation methods consist of separating the PCM from its environment so that it does not disperse in its liquid phase and be stable. There are three types: macroencapsulation, when the containers that wrap the PCM particles are of a considerable size (>1 mm in diameter); microencapsulation, if particles have from 1 to 1000 µm in diameter; and the newest, nano-encapsulated, with particles smaller than 1000 nm in diameter [93]. The smaller capsules are, the greater the surface-area-to-volume-ratio is, and, heat transference is consequently improved.

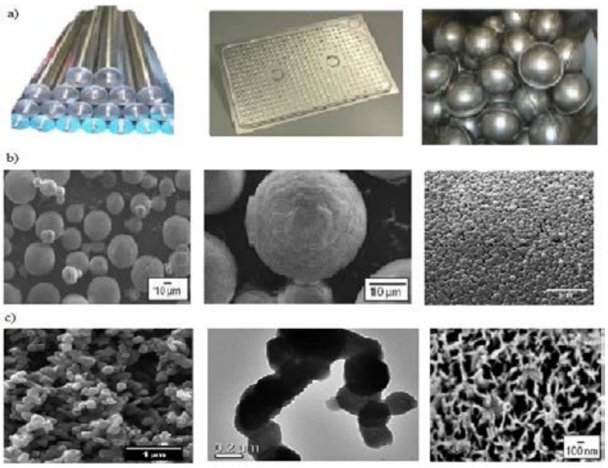


Figure 20. Examples of encapsulation methods: a) macroencapsulation in tubes, panels and spheres [91]; b) microencapsulation [95, 117]; c) nanoencapsulation [117, 118].

In the case of macroencapsulation, the bulk or core material is embedded in different types of containers (i.e. metal panels, spheres, cylinders, rectangular, granules, tubes, etc.), as illustrated in Figure 20-a. Macroencapsulation facilitates the transport and handle, offers design flexibility, improves the PCM compatibility with the surrounding and controls the external volume changes [95]. On the contrary, the thermal conductivity is not enhanced by this means. In the last decade, PCM has been developed and studied the fabrication of shape-stabilized forms, normally mixed with polymers as supporting materials (high-density polyethylene, styrene and butadiene) [119]. Its application does not require for any additional element; whereas the PCM gradually degrades inside the capsule due to segregation.

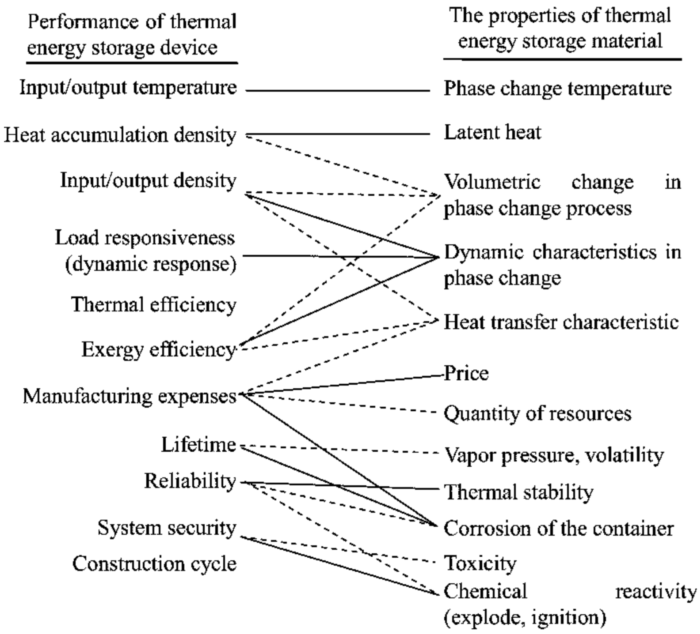
In order to avoid the material segregation, leakage and corrosion, micro and nanoencapsulation stand as the best alternatives. A typical structure for the two latter is composed of core and shell layers, which can be classified in mononuclear, polynuclear or matrix type. Microencapsulation is the process of individually coating particles with a continuous film to produce micrometre-sized capsules. It is composed of the bark layer and the PCM core, generally with a weight composition ratio of 20-80%, respectively. The morphology of microencapsulation presents different shapes (tubular, oval irregular or spherical, Figure 20-b) and they can be used as powders, pastes and slurries. Some of the advantages offered by this method is a controlled thermal energy release, improvements in compatibility, prevention of material exchange with the external environment, protection against degradation during heat uptake/release cycles, as well as a volumetric control during the phase change, increased PCM surface area and heat conductivity [94, 120]. Reducing the capsule diameter to the nanosized range would enormously enhance these beneficial effects. Some examples of nanoencapsulation are depicted in Figure 20-c, through scanning electron microscopy images.

The different methods for nano and microencapsulation are categorized into physical, chemical-physical and chemical; which can produce much smaller encapsulated PCM particles and the most used process is polymerization [121]. On the other hand, physical methods are limited by their granulated sizes and some examples of these methods include emulsions, coating, spray cooling, spray drying and fluidized bed processes [97].

2.2.5 Selection of PCM

Material selection is the core and most important step in designing LHS. The performance of the selected materials in various aspects will directly affect the TES ability and thermal storage/release efficiency. Table 3 illustrates the relationship between the performance of the heat storage device and the properties of the heat storage materials [122]. The diagram shows that the performance of the heat storage device and the properties of the heat storage materials are intertwined and significantly influence one another (straight lines indicate strong and direct relationship, while dash lines indicate a more indirect but also important influence).

Table 3. Relationship between heat storage performance and material properties [122].



- **Suitability of PCM properties and characteristics**

The selection of the suitable material is a key aspect and it must be based on the working temperature conditions, as it was reported by Iten and Liu [123]. In addition, other PCM properties are also important for the heat flux behaviour, such as conductivity [124]. Furthermore, Kaizawa et al. [106] reported the relevance of the PCM density and highlighted that it should be taken into account in order to optimize the volume and mass of the system. The PCM choice requires careful examination of the thermo-physical, kinetic, chemical, economic and environmental properties. Below, it is presented a list of the most relevant characteristics that an appropriate PCM would be desired to have, based on the literature [38, 39, 43, 55, 88, 110, 125, 126].

- Thermo-physical:
    - Melting temperature in desired operation or application range.
    - High latent heat of fusion.
    - High thermal conductivity.
    - Moderate density to avoid large volumes and heavy systems.
    - Minimal volume changes during phase transition.
    - High specific heat for additional sensible heat contribution.
    - Congruent melting and solidification, without phase segregation.
    - Little or no sub-cooling during freezing.
- Kinetic properties
    - Sufficient crystallization growth rates.
    - High nucleation rates to avoid changes in the stoichiometric composition.
- Chemical:
    - Long term chemical stability.
    - Capable of completing reversible freezing/melting cycle.
    - Non-corrosive, to be compatible with container or surrounding materials.
    - Non-flammable, no fire hazard and non-explosive.
    - Low degradation after long-term thermal cycles.
- Economic:
    - Cost-effectiveness.
    - Long life to avoid frequent replacement and maintenance.
    - Available in large quantities.
    - Easy access and transportation.
- Environmental:
    - Non-toxic, non-polluting.
    - Recyclables.
    - Non or low environmental impact.

The application of the PCM-based systems in high temperature industrial processes is not widespread due to technical barriers. PCM-TES at high temperature levels have only been tested at lab scale [37, 127, 128] and there are very few PCM products meeting the strict requirements to be commercialised [129]. Furthermore, there remains a lack of research owing to the mentioned technical and economic implications under real conditions and an unclear knowledge about the PCM thermal performance at high temperatures in industrial applications [37]. The major limitations are the long-term stability, corrosion and oxidation in contact to other materials, low thermal conductivities of non-metal PCMs, density changes, issues with congruent melting/solidification and the cost-effectiveness from the techno-economical perspective. For instance, the chemical constituents in exhaust gases interfere with heat exchange, compatibility and safety issues; the low stability of the physical and thermal properties of the materials and the corrosion between the PCM and the container [43, 98]. Besides, the PCM choice strongly influences on high operation and maintenance costs [70]; not only the material itself but also its container, operational control and the safety requirements. In this sense, several studies are focused on thermal cycling testing, material compatibility, PCM encapsulation and finding new materials [130].

It is worth mentioning there are no PCM that fulfils all the desirable properties to date. Therefore, a compromise needs to be made among the available candidates for a given thermal energy storage application, assessing the strengths and weaknesses. It is crucial to perform an exhaustive selection process considering not only thermo-physical properties, but also materials cost, availability and their facilities requirements. As a summary, the main properties for each PCM type are defined in Table 4, which gathers the conclusions brought by extensive reviews, theory and studies previously exposed in the section [43, 55, 71, 91, 94, 111, 131-133].

Table 4. Properties comparison of different PCM groups.

	ORGANICS		**INORGANICS**		**EUTECTICS**
	Paraffins	**Non paraffins**	**Hydrated salts**	**Metals**	**Org/Organic Org/Inorganic Inor/Inorganic**
Formula	C_nH_{2n+2} (n=12-38)	$CH_3(CH_2)_n COOH$	$AB \cdot nH_2O$	–	Mixes
Phase change temperature (ºC)	0–80	8–220	8–360	28–1077	-3–950
Latent fusion heat (kJ/kg)	170–268	86–352	31–380	15–388	26–757
Characteristic	Melting point and latent heat increases with the length of the chain. The most commonly used as commercial PCM.	Fusion in a wide range of temperatures and high latent heat	The oldest and most studied. Alloys of inorganic salts and water	High density and temperature. Increasing at commercial level	Composed by two or more different components and different PCM types
Cost	Low cost	Medium cost	Low cost	High cost	High cost
Advantages	Congruent fusion with no tendency to segregate phases Low or no subcooling Chemical and thermal stability		High phase change enthalpy High thermal conductivity		High heat of fusion per unit volume. High conductivity
	Chemically stable Non-corrosive Compatible with all metal containers Availability in a wide range of temperatures	Phase transformation marked High heat of fusion compared with paraffin	Easy availability Marked melting point Less volume variation than others High density Compatible with plastics	High heat of fusion per unit volume.	It melts and solidifies without phase segregation
Disadvantages	Low enthalpy of phase change Low thermal conductivity Flammable. It must not be exposed to excessively high temperatures, flames or oxidizing agents		Subcooling Corrosion Phase separation Segregation of phases		
	The melting point is not well defined. High volume variation	Slightly corrosive Varied level of toxicity	Corrosion according to the metal container Due to the high density, salts are	Low heat of fusion per unit of weight	Low heat of fusion per unit of weight

	ORGANICS		INORGANICS		EUTECTICS
	Paraffins	**Non paraffins**	**Hydrated salts**	**Metals**	**Org/Organic Org/Inorganic Inor/Inorganic**
	Not compatible with plastic containers	Unstable at high temperatures	deposited and reduce the active volume Slightly toxic	Under specific heat High weight	
Examples	n-tridecane n-trioctane n-heptadecane	acetic acid, stearic acid, lauric acid, esters, glycol, bee wax	$CaCl_2·6H_2O$, $Na_2SO_4·10H_2O$, $MgSO_4·7H_2O$	Galium	Na_2SO_4+NaCl+KCl+H_2O, NH_2CONH_2 +NH_4NO_3 , Capric acid, Miristic acid, Bi–Pb–In eutectic

Additionally, as a result of the literature review carried out during the thesis, it is possible to find tables in the Annexe 2.1 that represent the PCM inventory (from below 0 and up to nearly 1000ºC) organised by typology, latent heat of fusion and melting temperature. The parameters necessary for a preliminary identification of the most appropriate material include the operating temperature required for the application and heat requirements (melting temperature and the heat of fusion). The purpose of these tables is illustrating simply and clearly the alternatives for a specific operation temperature, based on the thermal capacity as a prior criterion. This serves as a first step to prioritise the PCM choice before a more refined selection, by discarding the non-suitable options until finding the best choice according to the rest of properties defined above.

- **PCM selection for working at high temperature ranges**

Even a more detailed investigation must be carried out in order to select materials exhibiting suitable properties at high temperature levels. As previously explained, most PCMs are highly corrosive to constructional materials, insufficiently thermally conductive, and have overly large volume expansion ratios during solid to liquid phase transition.

In general, PCMs can be divided into divided into four categories classified by phase change temperature [69]: cold temperature (below 20ºC), low temperature (20–100ºC), middle temperature (100–250ºC), high temperature (above 250ºC) and ultra-high temperature (above 1000). In the cold storage, the most representative applications are for chilled water, coil pipe and ice slurry cooling. Low temperature TES gathers uses such as space heating, domestic appliances (energy for laundry, bathing, washing, etc.), solar domestic hot water, seasonal storage and passive heat storage. Typical applications for the middle range are some industrial waste heat processes like drying, steaming, cooking, sterilizing, boiling, etc. Finally, the highest operational range is devoted to providing TES for thermal power generation (especially concentrated solar plants) and also other industrial process at high temperature level, namely smelting, melting, heating treatment, refining, incineration, etc.

As a summary, Figure 21 presents the PCM classification that can be used for applications ranged between -100 to 800ºC [70]. Thereby, melting temperature vs. latent heat of fusion capacity of all these materials are plotted divided into groups in function of the PCM nature and chemical composition. According to the temperature range defined above, the organic PCM materials and salt-water solutions are suitable for the cold and low temperature levels. Nitrates and hydroxide storage materials are the main TES materials in the medium range. Finally, hydrated salts, carbonate, chloride and fluoride materials are the most suitable in the highest range. In Table 5, PCMs at high temperature level are gathered from the tables in Annexe 2.1.

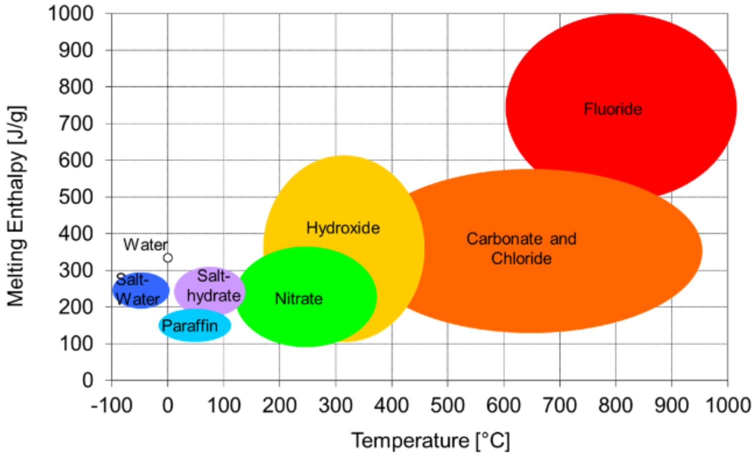


Figure 21. Classification of PCM with their melting temperature and enthalpy, based on [134].

Table 5. PCM melting at high temperatures and latent heat capacity.

Group	Sub group	PCM	Composition	Code	T_m (°C)	LH cap. (kJ/kg)	Ref
Inorganic	Hydrated salts	$LiNO_3$		I-SH57	252	380	[135]
		$NaNO_2$		I-SH58	270	200	[135]
		$NaNO_3$		I-SH59	303	177	[136]
		$RbNO_3$		I-SH60	312	31	[40]
		NaOH		I-SH61	318	165	[137]
		KNO_3		I-SH62	333	266	[108]
		KOH		I-SH63	360	134	[108]
		$CsNO_3$		I-SH64	409	71	[83]
		AgBr		I-SH65	432	49	[83]
		LiOH		I-SH66	462	873	[83]
		$PbCl_2$		I-SH67	501	79	[83]
		LiBr		I-SH68	550	203	[83]
		$Ca(NO_3)_2$		I-SH69	560	145	[83]
		$Ba(NO_3)_2$		I-SH70	594	209	[83]
		$Sr(NO_3)_2$		I-SH71	608	221	[83]
		LiCl		I-SH72	610	441	[83]
		CsBr		I-SH73	638	105	[83]
		$CsCl_2$		I-SH74	645	121	[83]
		$FeCl_2$		I-SH75	677	338	[83]
		RbBr		I-SH76	692	141	[83]
		CsF		I-SH77	693	143	[83]
		$MgBr_2$		I-SH78	711	214	[83]
		$MgCl_2$		I-SH79	714	454	[83]
		RbCl		I-SH80	719	198	[83]
		Li_2CO_3		I-SH81	732	509	[83]
		KBr		I-SH82	734	215	[83]
		$CaBr_2$		I-SH83	736	145	[83]
		NaBr		I-SH84	749	255	[83]
		KCl		I-SH85	771	353	[83]

		$CaCl_2$		I-SH86	772	253	[83]
		RbF		I-SH87	774	248	[83]
		NaCl		I-SH88	802	482	[83]
		PbF_2		I-SH89	824	60	[83]
		LiF		I-SH90	845	1044	[83]
		Na_2CO_3		I-SH91	854	276	[83]
		Li_2SO_4		I-SH92	858	84	[83]
		KF		I-SH93	858	468	[83]
		Na_2SO_4		I-SH94	884	165	[83]
		K_2CO_3		I-SH95	897	236	[83]
		$BaCl_2$		I-SH96	961	76	[83]
		K_2CrO_4		I-SH97	973	170	[83]
		NaF		I-SH98	996	794	[83]
		$PbSO_4$		I-SH99	1000	133	[83]
	Metals	Bismuth		I-IN27	271	53	[138]
		Pb		I-IN28	315	21	[136]
		Zn		I-IN29	419	112	[139]
		Zn_2Mg		I-IN30	588	230	[88]
		Mg		I-IN31	648	365	[139]
		Al		I-IN32	661	388	[139]
		Mg_2Cu		I-IN33	841	243	[88]
		Cu		I-IN34	1077	71	[139]
Inorganic Eutectics	Inorg. Eutectics	$LiNO_3$–NaCla	93.6/6.4	E-II49	255	354	[88]
		LiCl–CsCl–KCl–RbCl	28.5/43.5/13.7/13	E-II50	256	375	[88]
		NaOH–$NaNO_3$	81.5/18.5	E-II51	257	271	[140]
		LiOH–LiCl	63/37	E-II52	264	437	[141]
		NaOH–$NaNO_3$	59/41	E-II53	266	278	[88]
		LiCl–$Ca(NO_3)_2$	59.15/40.85	E-II54	270	167	[142]
		LiOH–LiCl	65.5/34.5	E-II55	274	339	[88]
		LiOH–LiCl–KCl	62/36.5/1.5	E-II56	282	300	[88]
		Na_2CO_3–NaOH–NaCl	6.6/87.3/6.1	E-II57	282	279	[140]
		NaCl–NaOH–$NaCO_3$	7.8/85.8/6.4	E-II58	282	316	[141]
		$NaNO_3$–NaCl–Na_2SO_4	86.3/8.4/5.3	E-II59	287	177	[142]
		NaF–$NaNO_3$–NaCl	5/87/8	E-II60	288	224	[143]
		KOH-LiOH	60/40 a	E-II61	314	341	[144]
		NaOH-NaCl-Na_2CO_3	77.2/16.2/6.6	E-II62	318	290	[140]
		LiCl-KCl-$BaCl_2$	54.2/39.4/6.4	E-II63	320	170	[88]
		KNO_3-KCl	96/4 a	E-II64	320	150	[144]
		LiCl-KCl-$LiCO_3$-LiF	47/47/3/2	E-II65	340	375	[88]
		KNO_3-KBr-KCl	80/10/10	E-II66	342	140	[144]
		LiCl-NaCl-KCl	43/33/24	E-II67	346	281	[144]
		LiCl-KCl	58/42	E-II68	348	170	[88]
		MnCl2-KCl-NaCl	45/28.7/26.3,	E-II69	350	215	[88]
		Li_2MoO_4-$LiVO_3$-LiCl-Li_2SO_4-LiF	27/25/23/18/6	E-II70	360	278	[140]

	$LiCl-LiVO_3-LiF-Li_2SO_4-Li_2MO_4$	42/17/17/12/12	E-II71	363	284	[88]
	NaOH-NaCl	80/20	E-II72	370	370	[144]
	$MgCl_2-NaCl-KCl$	55/25/20	E-II73	385	405	[88]
	$MgCl_2-NaCl-KCl$	45.4/33/21.6	E-II74	385	284	[88]
	$KCl-MnCl_2-NaCl$	45.5/34.5/20	E-II75	390	230	[88]
	$MgCl_2-NaCl-KCl$	50/30/20	E-II76	396	291	[88]
	$MgCl_2-NaCl-KCl$	51/27/22	E-II77	396	290	[88]
	$Li_2CO_3-K_2CO_3-Na_2CO_3$	32.1/34.5/33.4	E-II78	397	276	[88]
	$KCl-MnCl_2-NaCl$	37.7/37.3/25	E-II79	400	235	[88]
	Zn-Mg	53,7/46,3	E-II80	340	185	[88]
	Zn-Mg	51/49	E-II81	342	155	[139]
	Zn-Al	96/4	E-II82	381	138	[88]
	$Li_2CO_3-K_2CO_3-Na_2CO_3$	32/35/33	E-II83	397	276	[144]
	Mg-Cu-Zn	55/28/17	E-II84	400	146	[88]
	Al-Mg-Zn	59/35/6	E-II85	443	310	[88]
	Al-Mg	66/34	E-II89	450	366	[122]
	Mg-Cu-Zn	60/25/15	E-II86	452	254	[88]
	Mg-Cu-Ca	52/25/23	E-II87	453	184	[88]
	Al-Si-Sb	86/10/4	E-II88	471	471	[88]
	Al-Mg	65/35	E-II89	497	285	[88]
	Al-Cu-Mg	61/33/6	E-II90	506	365	[88]
	Al-Si-Cu-Mg	64/5/28/2	E-II91	507	374	[88]
	Al-Cu-Mg-Zn	54/22/18/6	E-II92	520	305	[88]
	Al-Cu-Si	68,5/26,5/5	E-II93	525	364	[88]
	Al-Cu-Sb	64/34/2	E-II94	545	331	[88]
	Al-Cu	67/33	E-II95	548	372	[88]
	Al-Si-Mg	82/13/5	E-II96	552	533	[122]
	Al-Si-Mg	83/12/5	E-II96	555	485	[88]
	Al-Si	88/12	E-II97	557	498	[88]
	Cu-Al-Si	49/46/5	E-II98	571	406	[88]
	Al-Cu-Si	65/30/5	E-II99	571	422	[88]
	Al-Si-Sb	86/10/4	E-II100	575	471	[139]
	Al-Si	92/8	E-II101	576	429	[122]
	Al-Si	88/12	E-II101	576	560	[139]
	Si-Al	80/20	E-II102	585	460	[139]
	Zn-Cu-Mg	49/45/6	E-II103	703	176	[88]
	Cu-P	91/9	E-II104	715	134	[88]
	Cu-Zn-P	69/17/14	E-II105	720	368	[88]
	Cu-Zn-Si	74/19/7	E-II106	765	125	[88]
	Cu-Si-Mg	56/27/17	E-II107	770	420	[88]
	Mg-Ca	84/19	E-II108	790	272	[88]
	Mg-Si-Zn	47/38/15	E-II109	800	314	[88]
	Cu-Si	80/20	E-II110	803	197	[88]
	Cu-P-Si	83/10/7	E-II111	840	92	[88]
	Si-Mg-Ca	49/30/21	E-II112	865	305	[88]
	Si-Mg	56/44	E-II113	946	757	[88]

Especially for high temperature TES, Fernandes et al. [145] developed a comparison of different possibilities available for energy storage. For temperatures around 400ºC, there are, currently, some materials such as the eutectic mixture of calcium chloride, lithium chloride and potassium chloride provides a high temperature PCM, with a theoretical latent heat capacity around 220 kJ/kg. Khare et al. [146] identified some metals and alloys, in particular, 88Al–12Si and 60Al–34Mg–6Zn, as potential candidate materials for very high-temperature LHS application in the range between 400–750ºC. Kotzé et al. [147] stated that the eutectic aluminium-silicon alloy, AlSi12, is an effective candidate material for a TES system; while the sodium–potassium alloy, NaK, was identified as an ideal HTF, however, it might be risky due to its reactivity to water. Liu et al. [144] reviewed PCMs with melting temperatures above 300ºC, which potentially can be used as energy storage media. In this range of temperature, it is common to find molten salts as a single component or mixed with other salts to form a PCM. Li et al. [83] reviewed the performance and enhancement of molten salt-based TES systems suitable for temperature range over 200–1000ºC. Their high densities and high latent heat values make them particularly effective PCMs. Nevertheless, PCMs working at higher temperatures (range of 800-1000ºC) is extremely challenging, i.e. PCMs based on carbonates and sulphates. As it was previously mentioned, molten salts are highly corrosive to several common metals, which would likely cause issues with encapsulation material and increases in the costs.

Other potential materials are the eutectic of magnesium and silicon (MgSi) or cupper based PCMs with a phase transition over 900ºC, however, the remaining thermo-physical properties are not reported yet. Undoubtedly, metallic PCMs have the advantage of a larger heat storage capacity and higher thermal conductivity. However, their poor performance in terms of liquid corrosion under high temperatures conditions results in poor compatibility with the container material, a crucial barrier when it comes to practical TES applications [83]. Besides, although some pure metals and metal alloys present interesting thermal properties to be used as PCMs in thermal storage systems, there is still a lack of consciousness about the implications of the metallurgical aspects related to melting and solidification of these materials under thermal cycling at high temperatures [139]. Therefore, these compatibility issues must be investigated further, followed by a systemic search for a reasonable encapsulation method.

Despite the potential of PCMs as TES, there is a shortage of studies about the implications under real conditions, insufficient database in terms of thermophysical properties, no reports in the assessment of the energy savings and an unclear knowledge about the PCM thermal performance at high temperatures in industrial applications [83]. Thus, the application of high temperature PCM in industrial processes will be further discussed in the next section.

2.3 PCM-TES applications

From the 1940s to the present time, the PCM trajectory has been studied by Rathod and Banerjee [71], who made a complete summary. The investigation of these materials did not receive much attention until the energy crisis of the 1970s and early 1980s, when it was widely studied for use in different applications, especially for solar heating. However, its use has been developed in recent decades as new features were discovered.

Given the wide range of melting temperature and latent heat of fusion, several authors including Abdin et al. [42], Abdin et al. [42] and Zalba et al. [43], developed extensive theoretical reviews of PCM applications. Similarly, Sharma et al. [55] summarise different investigations and analyse available TES systems that incorporate PCM for use in different applications. Its uses are found in construction [38, 95] and insulation [148], building climatization [149] (heating and sanitary hot water), thermal storage in solar energy [71], transport [43, 94], industrial processes to recover waste heat [44, 150], cooling of electronic components and motors [151, 152], food industry (food preservation), medicine (blood transport, hot-cold therapy) [69] and chemistry (reduction of exothermic peaks in reactions). As a summary, Table 6 gathers the potential applications and sectors where PCM can be applied as TES.

Table 6. Review of potential PCM storage applications and sectors with the operating temperature range [73].

Sector and Application	Temperature range (ºC)
Heating and Cooling	-40 to 350
Cold production	-40 to -10
Space heating and cooling of buildings	18 to 28
Heating and cooling of water	29 to 80
Absorption refrigeration	80 to 230
Adsorption refrigeration	-60 to 350
Transportation	-50 to 800
Cabin heating and refrigeration	-50 to 70
Battery and electronic protection	30 to 80
Exhaust heat recovery	55 to 800
Thermal protection	-269 to 130
Electronic devices thermal protection	25 to 45
Chips thermal protection	85 to 120
Data centres thermal protection	5 to 45
Spacecraft electronics thermal protection	-269 to 130
Food thermal protection	-30 to 121
Biomedical applications	-30 to 22
Solar energy	20 to 565
Solar cooling	-30 to 250
Solar energy storage	20 to 150
Solar power plants	250 to 565
Industrial waste heat recovery	30 to 1600

2.3.1 Heating and cooling

In order to improve the energy utilisation efficiency, the PCM-based LHS is rather useful for building owing to its high storage density. Zhang et al. [153] analysed different PCMs applied in the construction sector as passive heating and cooling. One of the most interesting PCM applications for buildings is to soften temperature variations and reduce the demand for heating and cooling. The concept known as free cooling developed by different authors [43], which consists of the cooling of the environment in buildings through the use of PCM, where the cold is used during the night to reduce the temperature in the hottest hours of the day. Some authors [132, 154] have experimented with impregnating PCMs in porous building materials, such as gypsum boards to improve thermal comfort. Up to now, PCM incorporation in opaque envelopment components has been well developed and includes a wide variety of applications [155], such as wallboards, floor tiles (Figure 22), concrete, bricks, mats, roofs, tubes and even shutters [156]. For instance, the PCM confined in the wall would absorb the heat during the hot day and then release heat at a cold day or night time [138]. Moreover, Weinläder et al. [157] published an evaluation of thermal behaviour, by experimental and numerical analysis, of three glazing systems filled with different PCMs. The results showed a reduction in heat losses and solar gains due to the PCM. The efficiency of a paraffin wax inside the glazing structure as a heat source showed a decrease of 20% in electricity consumption during winter [158].

Figure 22. Examples of PCM as construction component: a) flat profiles installed under floor to store and release thermal energy [155]; b) PCM integrated into transparent elements or windows.

Apart from using PCMs as a construction component, Tyagi and Buddhi [159] carry out an exhaustive review of the different methods for heating and cooling, such as PCM incorporation as part of the radiating floor. Moreover, PCMs can be also integrated into domestic refrigerators or freezers to achieve an improvement in the operational performance. For instance, freezers integrated with PCM storage were reported to provide energy saving up to 12% and COP improvement up to 19%, along with the resulting emission mitigation [160].

2.3.2 Transportation

It is also possible to create mobile TES, so that the system can be transported even off-site, far from where the heat was recovered. Marco Decker et al. [161] tested a pilot mobile prototype of 1.3 MWh, which discharged heat at a constant temperature, which consists of salt hydrate with a phase change temperature of 58ºC in a thermally insulated container. Tay et al. [162] experimentally studied a TES system based on tubes inside a PCM filled cylindrical tank. Additionally, Guo et al. [163] reported a mobile-TES system used to supply heat for distributed heat users. [164] designed mobilized TES systems with erythritol as PCM, which can be used for industrial heat recovery and distributed heat supply (Figure 23), and experimentally investigated heat charging/discharging performance.

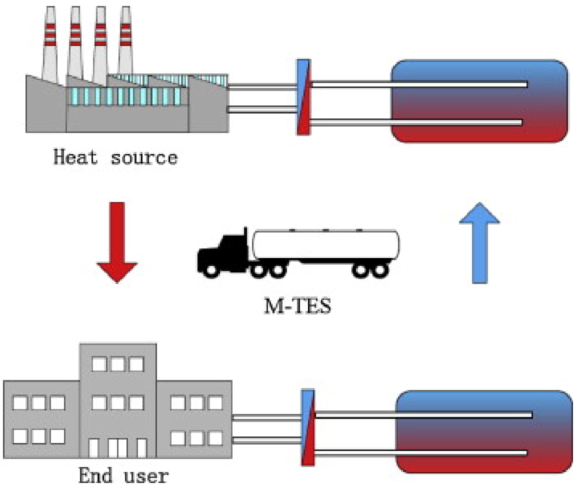


Figure 23. Diagram concept of a mobile TES system used for waste heat transport [164].

In this sense, temperature control is required while shipping of food and perishables, pharmaceutical distribution containers and blood transport, among others. These kinds of applications are very suitable for PCM-based passive TES techniques. In the food industry, the rise in external temperature increases the rate of deterioration or causing deterioration or caused discarded products. In order to sustain the cold as long as possible, conventional insulation is combined with PCM where cold can be stored as latent heat to make it last longer [69].

2.3.3 Thermal protection and management

In recent years, PCMs have been widely used as an alternative cooling method to avoid degradation by peak temperatures for various applications such as electronic equipment, portable phones or engines in the automobile sector. The passive thermal management that PCMs offer can be used when heat dissipation is periodic or sudden transient. A PCM finned radiator-fan was proposed to prevent microprocessor from overheating in case of transient heat load (the concept of dissipation is illustrated in Figure 24). For a typical commercially available flash memory, the temperature was dramatically reduced by applying gallium as PCM [138]. Gumus and Ugurlu [165] developed an experimental TES system for preheating internal combustion engine with $Na_2SO_4{\cdot}10H_2O$ as PCM. In an ambient condition of 2ºC, the TES system helped maintain the engine at an average 17ºC. This demonstrates the potential of PCM cooled heat sinks in case of intermittently used electronic devices where there is adequate time for PCM to solidify between usages.

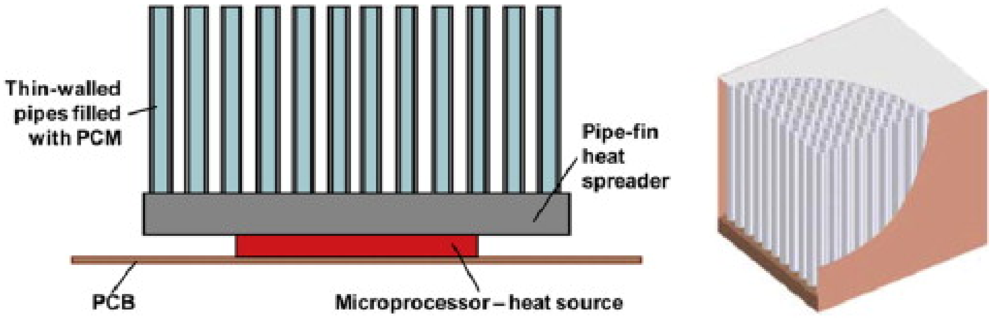


Figure 24. Heat dissipation for electronics cooling with pipe-fins filled with PCM [138].

Furthermore, it has been proven that incorporating PCM microcapsules into a textile structure can change and improve its thermal performance. PCMs present a very suitable transition temperature point or range between 18ºC and 28ºC, which is also the human comfort temperature zone. Thus, textiles with PCM help to avoid extreme temperatures absorbing and releasing a large quantity of latent heat in a narrow temperature band of phase change, suitable for the human body [138].

2.3.4 Solar energy storage and generation

PCM storage has great potential for use in the field of solar energy and it can be integrated for various purposes such as heat, cold, steam or electricity generation [71]. Most of the applications have been found in hot water or steam generation processes in solar plants [104, 166-169]. Depending on the storage capacity the uses are different, i.e. a small storage capacity allows to produce electricity only when the sunshine is available; in an intermediate load configuration, solar energy is collected during the daytime to be later used during night-time or demand peaks; and finally, in a large continuous mode, demand may be covered between longer periods [170]. Additionally, combining these heat storage systems with solar collectors and heat pumps can bring significant advantages for decreasing energy consumption. Considering a proper design and configuration for hot domestic water, a reduction in tank volume up to 40% can be obtained without compromising the solar fraction [171]. Regarding the energy generation, the performance of solar power plants can be enhanced by means of PCM application as TES (as depicted in Figure 25) by reducing the mismatch of solar supply and energy demand periods [75].

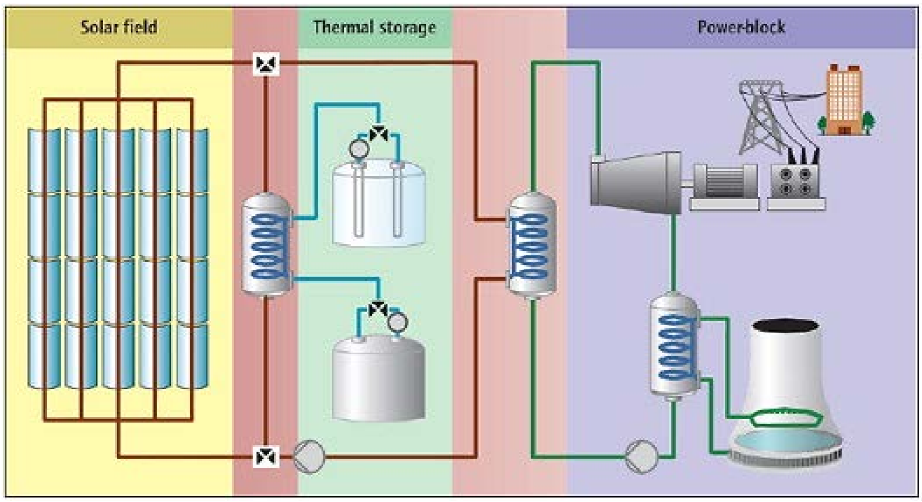


Figure 25. Diagram of a potential integration of TES system in a thermal solar plant [170].

Another example is the performance improvement for water storage due to a transparent insulating material layer as an additional covering for the collector [74]. High temperature PCMs having melting temperatures of 300–550ºC have the potential to be employed as energy storage media for TES in concentrated solar power plants [138]. For instance, the molten nitrate salt combining 60 wt% of $NaNO_3$ and 40 wt% KNO_3 is used as storage medium within this temperature range [170]. Apart from that, the application of these smart materials should be highlighted in thermal solar [172], photovoltaic modules [173], and also the combination of both in photovoltaic/thermal systems [174]. When PCMs change phase can reduce the operating temperature of photovoltaic panels and the energy output increases due to this passive cooling [87]. In addition, PCM has also been applied in the cooling applications, namely, in solar cookers [138] or solar absorption refrigeration systems [175].

2.3.5 Industrial waste heat recovery

Over the past century, awareness of the environmental sustainability principle has been increasing worldwide and has become deeply rooting in the culture of companies and industries. Currently, the EII is facing numerous requirements and initiatives aimed to meet environmental targets [6]. These EII sectors, composed by aluminium, cement, mineral, steel, iron, ceramic, glass, pulp, paper and chemical industries, among others; are making significant efforts to decarbonise their sectors following the 2050 roadmap for energy [176] and achieving the environmental challenges, i.e. those expressed in the Paris Agreement [177]. Meanwhile, industrial producers are conscious of energy costs, as these can be considerable in the overall production cost distribution. For instance, in the ceramic sector, the overall average energy cost can be as much as 30% of total production costs [178]. EII should grow while being economically competitive in terms of energy efficiency and environmental performance, towards exemplarity in a more sustainable industrial future. To do so, these industries aim for overall optimisation, energy and resources efficiency, minimising residues and heat losses by means of WHR, which is one of the next frontiers for EII in terms of energy efficiency [33, 179].

The industrial sector accounts for one third of the total energy consumed in society, of which a substantial part eventually becomes waste heat owing to inefficiencies. It represents 20% of the European industrial heat demand, from which a 50% correspond to temperatures over 250ºC [53]. The most common waste heat streams may be gases (including exhaust gas, flaring gas, steam and hot air), liquids (such as hot oil and refrigeration water) and solids (for example, waste and products) [180]. Examples of typical heat sources are melting and heating furnaces, boilers, incinerators, thermal treatments and steam distributions. All of these represent the possibility to recover heat, otherwise wasted or simply released to the environment. WHR has a direct effect on the efficiency of the process, and consequently, achieving reductions in consumption, in pollution, in equipment size and costs [78]. Some of waste heat losses are inevitable; however industrial facilities could reduce additional losses by improving the efficiency of their processes and equipment or incorporating WHR and storage technologies [181]. Waste energy in terms of heat can be recovered and reused in another plant process or even outside the plant for different purposes depending on the heat quality. For example, the most common uses are combustion air preheating, charge preheating before entering the furnace and supplying energy to other upstream and downstream processes. The working temperature range of the EII achieves very high levels, as illustrated in Figure 26 [14].

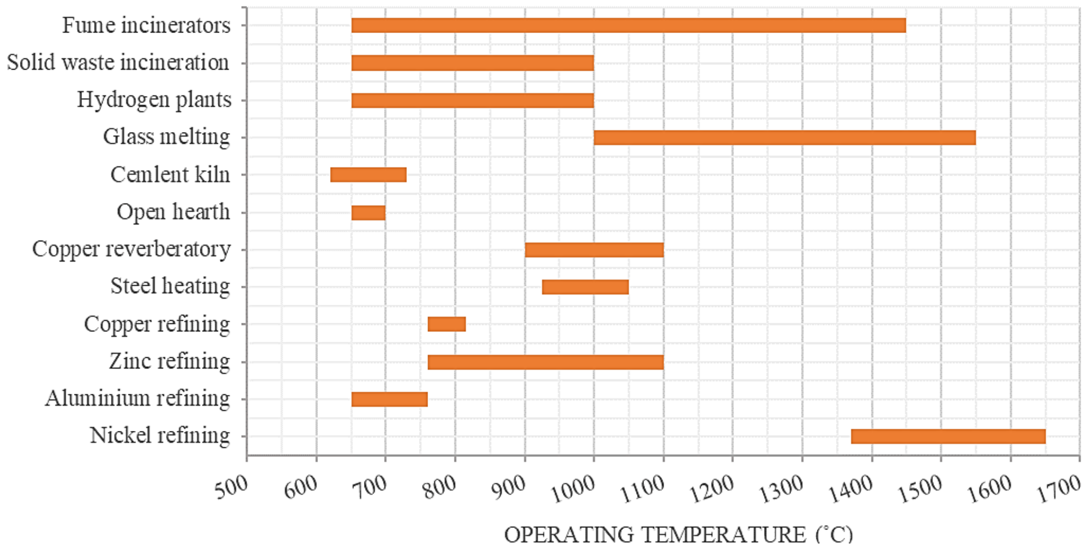


Figure 26. Typical operating temperature range of different EII processes (adapted from [182]).

Under this scenario, different WHR technological solutions are based on systems such as conventional heat exchangers (HX), TES systems, recuperators, regenerators, heat wheels, heat pumps, steam boilers, cold power production, organic Rankine cycles, thermo-chemical/biological reactions, etc. [181, 183, 184]. For instance, recuperators, the most used equipment, can save up to 25% of energy [185]. Nonetheless, very little attention has been paid for TES integration at those applications up to now. Despite all these benefits, approximately 4000 TWh of heat is wasted every year worldwide, whilst in Europe alone, the reduction potential could be a total of 250 million tons CO_2 emissions per year [186]. In that sense, only about 5% of the final energy consumption is assumed to be used by TES in industrial installations [62]. Thus, there is a significant opportunity to establish advanced TES technologies capable of storing waste heat and avoiding the consumption of other energy resources to produce heat [187].

To this end, LHS systems have emerged as an attractive option for managing the wasted thermal energy in particular, since it increases energy efficiency through improved use of waste heat as well as balancing intermittencies between the availability and demand of thermal energy. TES is the temporary storage of high or low temperature energy for later use. It bridges the time gap between energy requirement and energy use. This is evidenced in the Oró et al. [49] paper, which is focused on numerical models comparing the thermal performance of two packed bed storage with PCMs at low temperatures. Bhagat et al. [188] numerically studied the thermal performance of multitube PCM-TES at medium temperatures (approximately 200 ºC) optimized with fins as conductivity enhancers. By properly selecting the PCM, LHS technology can be used also in the temperature range of 300 to 400ºC [189]. $NaNO_3$ is a typical example of inorganic salt used within this range [190], as in the system designed and tested by [191] represented in Figure 27. Another peculiar example is a combination of a deformable copper shell filled with a mix of KNO_3-$NaNO_3$ can be used as encapsulated PCM [192].

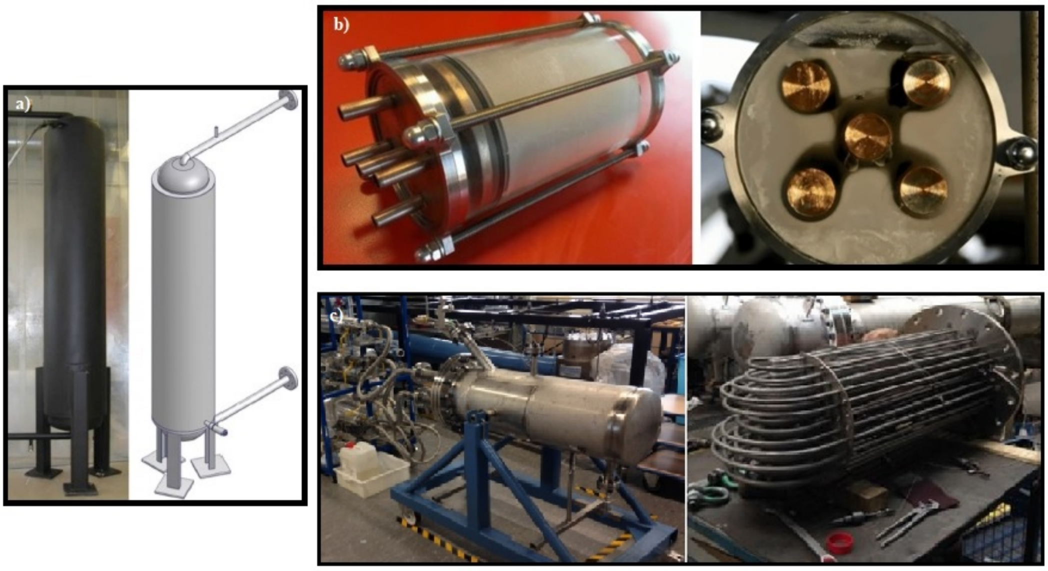


Figure 27. Example of lab prototypes: a) $NaNO_3$ storage test module [191]; b) shell-and-tube configuration with 5 PCM tubes; c) multitube configuration with $MgCl_2·6H_2O$ as PCM [193].

Lin et al. [194] highlighted the existing gap between theoretical researches and practical operations. Although several studies for design and modelling PCM-TES have been published [65, 195-197], and some of these materials have been tested at the laboratory scale [55, 127, 128, 198]; their applications are scarce at industrial levels. Only a few LHS design concepts have been tested in pilot plants to assess their performance with high technology readiness level (TRL 7) and even less meet the requirements to be fully commercialised. Furthermore, there remains a lack of research owing to the mentioned technical and economic implications under real conditions, no reports in the energy savings assessment and an unclear knowledge about PCM thermal performance at high temperatures in industrial application [37].

Recently, a large scale lab prototype PCM-TES around 5 kW power was built and tested, proving that $MgCl_2·6H_2O$ is an interesting PCM for industrial applications, due to its high melting point of 117 ºC [193]. However, most of the applications have been found in hot water or steam generation processes in solar plants [104, 166-168]. It is even more complicated to find results at higher temperature ranges, since most PCMs are highly corrosive to constructional materials, insufficiently thermally conductive, and have overly large volume expansion ratios during solid to liquid phase transition. Only a few demonstrators of high-temperature LHS has been constructed and operated over 200ºC, due to the high cost of experimental test and model validation with experimental data under real conditions [160]. Among the studied prototypes, Michels and Pitz-Paal [108] experimentally tested a cascaded storage system with three alkali nitrate salts as PCMs, within a range of melting temperatures between 306 and 335ºC. The cascade of multiple PCM systems, which are marked by a minimum of necessary storage material, shall ensure the optimal utilization of the storage material. Scharinger-Urschitz et al. [199] presented an experimental investigation of a PCM storage describing the enthalpy function and compared against theoretical studies. Sodium nitrate is used as PCM and the storage is operated ±30ºC around the melting point (306ºC). Values for the apparent heat-transfer coefficient are derived, which allow capacity and power estimations for industrial scale LHS-TES. Another example is a PCM-TES of 700 kW power system, based on sodium nitrate with one hour of storage capacity, which has been recently installed in Spain [64].

One step behind, high-power systems remain in research and development with some demonstration projects at TRL 4-5 [64]. One of the major issues with high temperature PCM-TES is that the required materials for encapsulation (refractory steel, extruded ceramics) are recognised to be expensive [40]. In contrast, their long lifetime upon charging-discharging cycles reduces the financial impact. Concretely, Kere et al. [200] studied the applicability of a TES system in the ceramic sector, where thanks to that, the consumption of other energy resources for heat production was avoided [103].

Figure 28. High temperature industrial PCM-TES prototype from DLR (700 kW-power) based on $NaNO_3$ salts installed in Spain [201].

In conclusion, all the studies agree on the necessity of further research on this line to overcome the current challenges, to increase the LHS technology maturity and to move forward the PCM integration at high temperature levels. To do so, the main objectives are aligned with it and developed alongside this thesis. Mainly, the design according to the heat demand and the waste heat recovery potential and the suitable selection of the storage material and system configuration. Furthermore, the assessment of the thermal performance is studied by means of the development of numerical and analytical calculations to reliably predict the PCM performance, especially in the high temperature range. Finally, the thesis eases the integration of the PCM-TES system along with the existing industrial processes and evaluates the applicability of the solution in different cases from the EII sectors and with different PCM materials.

«Sólo se mantiene una civilización si muchos aportan su colaboración al esfuerzo. Si todos prefieren gozar el fruto, la civilización se hunde»

José Ortega y Gasset

«Have no fear of perfection: you will never reach it»

Marie (Sklodowska) Curie

10 - CONCLUSIONS AND FUTURE WORK

10.1 Final conclusions

The main goal of this thesis addresses the implementation of an innovative TES based on PCMs, working at high temperatures, to recover and store waste energy.

The results and conclusions obtained along this thesis respond successfully to the general and specific objectives stated in chapter 1. In this sense, the proposed PCM-TES solution allows not only transferring heat, but also to store thermal energy from heat sources detected in different intensive energy industries. Specifically, the PCM-TES design uses high temperature exhaust gases to raise the PCM temperature above its melting temperature. Then, the heat causes the transition from solid to liquid state by accumulating latent heat of fusion, instead of working only with the sensible heat. It aims at increasing up the air flow temperature used for fuel burning in furnaces and other heating processes, both upstream and downstream. Consequently, a reduction in the fossil fuel consumption is achieved in conventional industrial heating processes. In this vein, implementing PCM-TES is a sustainable and innovative option to increase the energy efficiency (5-10%) and to reduce the environmental impact associated.

To do so, firstly it was expected to develop a conscientious investigation of the potential use of PCM at high temperature to recover energy from industrial furnaces and hurdle the implications in waste heat recovery characterised by high variability of flows and temperatures.

On the one hand, a detailed evaluation of PCMs and its application is highlighted in different fields, as industrial heating, construction, climatization, solar energy, transport, electronics cooling, medicine, food preservation, and chemical processes. The PCM suitability was assessed in chapter 2 in terms of thermophysical properties and also materials cost, availability, hazard issues and the facility requirements. Additionally, during the review, more than 500 PCMs were plotted showing the most relevant properties (melting temperature versus latent heat of fusion capacity) and divided into groups in function of the chemical composition. Especially, 82 PCMs at high temperature level (250-1000°C) were identified as potential alternatives for the thesis target, being the hydrated salts, carbonate, chloride, and fluoride materials the most suitable in the high range. As a first conclusion, it is detected a lack of available suitable materials for high temperatures in comparison to lower and medium levels.

Focusing on this high temperature range, the alternative TES technologies review conclude that the latent heat-based technology presents an efficiency ranging from 75 to 90% for operating temperatures in a wide range (up to 900-1000°C) and the associated cost is between 10 and 70 €/kWh. Thus, the LH systems based on the use of PCM meets the compromise between innovation and viability potential. Although there are some lab-scale prototypes, it was found that its implementation under real operational conditions is still limited. Hence, consolidating this technology at large-scale and under real conditions is a priority for its further development and commercialisation.

On the other hand, the material's ability to store and transfer heat depends strongly on the PCM thermal properties, which are namely latent heat, melting temperature, specific heat, thermal conductivity, durability and cyclability. It was demonstrated that the accurate overview and measurement of the thermal properties of PCMs is critical to any process or material that undergoes a large temperature and/or phase change. Accordingly, a review of the available characterisation equipment and methods to measure the thermophysical properties of PCMs was performed in chapter 3. Concerning experimentation, it was concluded that the DSC is the most important analysis technique employed to study PCMs, followed by the TGA and DTA and T- History method. Regarding thermal conductivity, the MTPS technique works properly for most PCMs in a range from -50°C up to even 500°C. However, it was concluded that the LFA method is more suitable for higher temperature PCM characterisation, namely metals and alloys.

Secondly, the thesis aimed to design, at conceptual level, the best configuration of PCM-TES solution by adapting the storage to the end-user facilities and the potential heat sources.

In this thesis, the original design system based on PCM starts from conceptual development, through design and basic engineering; and finally, to have it ready for its integration into an industrial plant under real operating conditions. Overall, the complete methodology, that addresses technical and engineering aspects, provides flexibility to select a design fully adapted to the operating framework of the EII sectors. Two study cases (ceramic and steel industrial plants) were chosen as representative of some of the most intensive energy consumer sectors with a great potential for WHR. The waste heat recovered from flue gases exits at high temperatures (750-1100°C) and the flow rates are between 640-785 Nm^3/h. The characteristics and thermal properties of the PCM were considered to design the equipment configuration taking into account the requirements for both ceramic and steel sector.

To achieve a successful implementation at industrial scale, available commercial PCMs are proposed to meet the end-user requirements. Two inorganic salt PCMs were selected as core storage material for both EII sectors and were experimentally characterised in chapter 3. For the steel industry, H500 was considered the most suitable PCM since testing revealed to have an appropriated melting point for this sector (509°C), high storage capacity (260 kJ/kg) and showed to be safe at temperatures up to 750-800°C. In the case of the ceramic industry, testing on H885 presented a higher latent heat (191 kJ/kg) and has the most desirable melting temperature (888°C) for the application. The stability tests revealed that the material, when sealed, is stable when exposed to the air atmosphere at temperatures below 950-1000°C.

The conceptual design is a starting point to face further technical and engineering aspects for a successful PCM-TES implementation at industrial level. Five different conceptual designs configurations were proposed in chapter 4. The alternative PCM-TES options were assessed by thirteen decision criteria, weighting technical, economical and design key aspects. To do so, an in-house MCDA is performed following a methodology based on the AHP. The beneficial and favourable aspects considering the adequacy to the application, the flexibility of the design and the configuration adaptation to accomplish a proper technical solution were highlighted with a positive value; while crucial drawbacks or with major difficulties in the performance/assembly were scored negatively to discard technical or economic unfeasible options. The most suitable configuration for the case study was a shell-and-tube configuration, with double concentric tubes filled with PCM.

Thirdly, the engineering process developed in this thesis expected to define sizing specifications and geometrical configuration of the PCM-TES main equipment, according to the different process requirements for each specific sector.

The engineering was carried out in chapter 5 by means of an iterative process to adjust the system configuration, according to the process requirements for each specific sector. The thesis allowed determining a set of design parameters, such as the diameter and number of tubes, the volume of the system, the construction materials and equipment costs, in order to achieve a consistent, efficient and feasible PCM-TES design. A sensibility analysis was used to find out the optimal tubes number and suitable sizing for each solution, achieving a good compromise among the technical, practical, and economic perspectives. These results served as a basis for the technical documentation, drawings and diagrams (namely instrumentation specification sheets, PIDs, layout of the solution at the plant, etc.) in the pursuit of a PCM-TES design to be implemented at industrial scale.

The case study in the ceramic industry is designed to recover waste heat at very high temperature levels (over 1100°C) from the furnace exhaust gases. The stored energy is meant to preheat the air temperature entering the furnace. Moreover, the PCM-TES is installed in vertical position for better mechanical stress resistance and easier cleaning and maintenance. The configuration consists of an external shell containing double concentric tubes of 2 m long and 600 mm in diameter, filled with 4700 kg of PCM. The obtained results prove the achievability of very high temperature levels in the combustion air preheating (over 700°C); so, corroborating an energy and environmental efficiency enhancement, compared to the conventional system with air outlet at 650°C. According to the material compatibility testing regarding the ceramic sector, a nickel-based alloy is needed because it presents resistance to creep and oxidation up to 1200°C, which resulted in an elevated material cost.

The case study in the steel sector recovers waste heat coming from a syngas torch at 800°C, which provides the necessary energy to charge PCM system solution during the periods where the gasifier is burning the syngas in excess. In this case, the number of the inner tubes was set in 7, with 3 meters long filled with PCM and 270 mm diameter, while the external shell diameter containing the tubes is around 1.5 meters. Considering technical issues for construction and the suitable thermal transfer, the PCM thickness was set at 35 mm. The construction material in the steel sector should be S/S 310 S (high amount of content of Cr), which resisted the attack of the salt compared to S/S 316, compatible with the PCM H500 and cost-effective.

Fourthly, another important objective was to model the thermal performance of the PCM-TES solution (charge/discharge, temperature profile) in order to select the most suitable construction materials.

Once the engineering was defined for both cases, a numerical model was developed in MATLAB® software to investigate the thermal performance in chapter 6. It was concluded that both convection and conduction are dominant phenomena during the PCM melting and solidification. The natural convection inside the concentric tubes, especially relevant during melting, is considered by an effective conductivity. In this sense, temperature profiles of the PCM and the HTF, as well as the combustion air temperature during the charge and discharge processes. The simulation results allow performing an appropriate design in material and sizing, ensuring the technical feasibility of these systems working at critical temperature ranges. The obtained results proved the achievability of high temperature levels in the combustion air preheating (from 700 to 865°C in the ceramic sector and from 300 to 480°C in the steel sector). The charging and discharging evolution were evaluated, resulting in long cycles (11-25 hours), significantly influenced by the low PCM thermal conductivity. The numerical modelling results serves, on the one hand, as active feedback and retrofitting output for the design parameters of the PCM-TES, which can be adjusted in the function of the model outputs. And on the other hand, the predicted thermal behaviour provides the core for the PCM-TES design validation, facilitates material selection at high temperatures and reduces the uncertainty risk in operational performance and on-site implementation at larger scales.

Fifthly, this thesis intends to develop of technical documentation and process specifications of the PCM-TES prototype by establishing the operating conditions and equipment necessary to achieve the level of reliability, efficiency and safety required.

Following the design thinking premises, chapter 7 allowed to achieve an innovative implementation of the industrial prototype. To do so, a comprehensive assessment was conducted to adapt and rescale the PCM-TES system in function of the steel sector requirements. As a result, the configuration of the system was redefined, by reducing the total heat transfer area and the number of tubes (6 tubes instead of 7); thus, the storage capacity of the system and PCM mass decreased (1400 kg of PCM). More detailed engineering for the prototyping was developed to provide technical documents, drawings and component specifications; indications of PCM system location, PID, peripheral equipment and supplies; equipment layout, connections and supply needs for the system integration to the plant; assembly, disassembly, maintenance, health and safety procedures and the filling procedure of the double concentric tubes with the salt PCM. In addition, the work performed developed the procedures for working operation (charge and discharge), set operating conditions and the instrumentation of the monitoring and control system to guarantee a ready solution for its further validation. Hence, the work developed help to boost the integration of an innovative system, overcoming the current lack of information of PCM-TES applications at industrial level, especially at high temperatures.

Sixthly, this thesis aimed to provide a prospective validation of the numerical model in chapter 6 and PCM-TES design of chapter 5.

To this aim, in chapter 8, two approaches of 3D numerical model were compared and developed to simulate the transient and energy behaviour of the PCM-TES system. The simplified in-house MATLAB® model provides results sufficiently reliable and less time consuming for practical application in the engineering and industry, and are preferred during the early stages of design. The COMSOL Multiphysics® model approach is more accurate and versatile to simulate multiphysics problems, conversely, it presents a higher computational time cost. Regarding PCM-TES performance, the results obtained stated the air combustion stream received 338 kWh of heat released by the PCM within 3 hours of discharge, providing an average temperature of combustion air in the range of 320-150ºC. During the charging, the PCM absorbed 351 kWh from the flue gas stream for 6 hours. The annual energy savings are 230 MWh, considering the 9-hour-cycle (charge + discharge) continuously applied in the mould heating process of the steel sector plant. Furthermore, the temperature distribution is assessed along the concentric tubes filled with PCM, to check that the operating conditions do not exceed the maximum working temperatures of the selected construction materials.

Seventhly, another specific objective was to probe the feasibility of a cross-sectorial approach by enlarging its replicability in many industrial sectors (ceramic, metal, chemical, glass, cement, and paper sector, among others) considering technical and economic aspects.

The flexibility of the PCM systems offers the opportunity to adapt the design to the plant specific requirements. In this sense, a simplified tool based on the MATLAB® model was developed in chapter 9 as a prefeasibility of the PCM-TES integration performance at an industrial plant from the environmental, technical, and economic perspectives. In this vein, the thesis conducted a parametric and sensitivity analysis to assess the techno-economic performance of the PCM-TES solution under different working conditions and EII sectors. A set of equations based on correlations among the most relevant parameters of the system performance were established as the core of a feasibility tool. As a result, it was demonstrated that the thermal conductivity, volume, and storage capacity of the PCM arise as the most influencing parameters. This tool can select a suitable PCM for the operating conditions and estimate the performance (PCM mass and volume, storage capacity, temperature obtained, energy savings, economic costs) of the PCM-TES design configuration described in the thesis.

A suitable design, material selection and sizing are crucial parameters to obtain energy and economic benefits. Besides, it strongly depends on the heat transfer rate and the time in which the energy must be stored or released according to the plant operating conditions. Thus, it was concluded that the PCM able to recover and transfer the heat more rapidly would increase the PCM-TES adaptability to a wider variety of process integration. Therefore, a review of metals and alloys was performed in chapter 9 in search of alternative PCMs for high temperatures, although there is a current lack of understanding of its commercial application and metallurgical implications. A multicriteria assessment was conducted with the tool outputs comparing metal alloys and inorganic hydrated salts. The inorganic PCMs presented higher net economic and energy savings (26400 € and 480 MWh/year, respectively). Even though the metal PCMs are around 10 times more expensive than the inorganic salts, very profitable savings/investment ratios were obtained, due to its storage capacity and fast charging and discharging. However, the use of metals involves higher impacts in the climate change indicator compared to molten salts.

Finally, the estimated return period of the PCM-TES system is calculated for several proposed case studies of a parametric study, changing PCM material, operation sector, design and sizing parameters.

In the ceramic sector, working at very high temperatures entails high equipment costs resulting in longer return periods (more than 30 years). This fact highlighted the technical and economic barriers existing in working at high temperature levels. While more acceptable payback periods are observed in the steel sector (between 5-8 years) with an energy efficiency around 10% during the PCM-TES discharge phase. This means up to 4% annual savings for the industrial plant), depending on the PCM and the design. Large companies from the energy-intensive industry have elevated gas consumption, which would mean an important economic benefit. In order to achieve higher saving ratios, the design, the process control and the integration within the overall system should be optimised. Also, the payback time and the investment costs will be considerably reduced if the PCM-TES system is manufactured at commercial stage, and not only as a stand-alone prototype.

To sum up, the overall results obtained along this thesis are a starting point for consolidating and promoting novel PCM-based technological solutions and materials in terms of research, innovation, and feasibility to be implemented at industrial scale. This topic is aligned with the scope of both the scientific and engineering community, such as innovative and intelligent materials and designs to optimise the performance of heat recovery and storage systems.

10.2 Future work and new research lines:

10.2.1 Material innovation

The following are recommendations for future research into materials to be used as PCMs for thermal energy storage:

• Investigation of new materials that have high thermal conductivity, such as metal alloys instead of inorganic salts. The metal PCM and its alloys offer, on the one hand, high thermal conductivity and volumetric energy density, which would involve a great potential for more flexible and fast charging systems. And on the other hand, they are more expensive and the integration in systems is complex due to the thermal expansion issues and the implications of operating at high temperatures, which would require ceramic containers for encapsulation.

• Since the main disadvantages of PCMs is its low thermal conductivity which requires a long time for the melting and solidification; optimisation strategies can be employed to enhance the heat transference rate of PCMs. Assessment of the integration of PCM embedded in metal foams or mesh structures, innovative materials, such as micro-encapsulated PCMs or nanomaterials.

• Selection of PCM with upgraded thermo-physical properties, proven by DSC characterisation and under thermal cycling to ensure their performance over several melting/solidification stages.

10.2.2 Design improvement

Thus, regarding future work, several studies to complement the work done and advance more in the design and simulation might address the following points:

• To perform a parametric analysis varying the number, length and sizing of tubes and the thickness of the PCM ring, in order to increase the heat transference and take more profit of the exhaust gases.

• Different design of the PCM-TES system configuration should also be taken into consideration to increase the efficiency and maintain the air combustion temperature on a constant level. For example, variation of the system geometry, locating the PCM material in solid tubes, creating different paths for the heat transfer fluids streams, etc.

• To assess the effect of vertical or radial fins in the PCM layer by means of the 3D model simulations varying the quantity, length and thickness of internal-external-arranged fins, operating temperature, sizing and fin materials.

• Investigation of the use of other heat transfer fluids having a thermal conductivity higher than that of air, or with particulates as doping material to increase its properties. However, this is restricted by the plant and process requirements.

• Dynamic batch cycle simulation with standby times should be run to understand how PCM would react on those periods and estimate the heat losses.

10.2.3 Industrial validation

An accurate experimental investigation could be carried out to study the behaviour and the thermal performance of PCM-TES under real operational condition at industrial scale. The results obtained in the simulations could be used for comparison with experimental data acquired from a pilot integration the PCM-TES in order to validate the proposed system. During the thesis development, several industries from EII sectors have shown great interest in this innovative technology for waste heat recovery in the industrial community.

Furthermore, the retrofeeding of the tool with variables measured directly from EII plants integrating PCM-TES systems would allow enhancing the tool response getting more accurate and reliable results for more industries and production conditions. To ensure the tool robustness, future work should analyse characteristics and parameters in the operating modes of the PCM-TES integrated system, under different working conditions (process temperatures, flows, cycle periods, volumes, etc.)

10.2.4 Inter-site synergies

Finally and all things considered, future work could focus on further use of the PCM-based system, not just on the same process where the heat is recovered. Therefore, the plant overall efficiency can be improved, even if the processes where the heat is generated and demanded are far from each other. Furthermore, the mobile TES strategy could be applied not only within the same plant, but also to extend its use between sites, increasing the industrial symbiosis of an industrial park.

«I've missed more than 9000 shots in my career. I've lost almost 300 games. 26 times, I've been trusted to take the game winning shot and missed. I've failed over and over and over again in my life. And that is why I succeed»

Michael Jordan

10 - CONCLUSIONES Y TRABAJO FUTURO

10.1 Conclusiones finales

El objetivo principal de esta tesis doctoral es la implementación de un innovador sistema de almacenamiento térmico basado en materiales de cambio de fase (PCM-TES), trabajando a altas temperaturas, para recuperar y almacenar calor residual.

Los resultados y conclusiones obtenidos a lo largo de la tesis responden con éxito a los objetivos enunciados en el Capítulo 1. En este sentido, la solución PCM-TES propuesta permite recuperar, transferir y almacenar energía térmica provinientes de fuentes de calor residual identificadas en diferentes industrias de energía intensiva (EII). Específicamente, el diseño del PCM-TES utiliza gases de combustión a alta temperatura para elevar la temperatura del PCM por encima de su temperatura de fusión. El calor provoca la transición del estado sólido a líquido, acumulando el calor latente de fusión en lugar de trabajar sólo con el calor sensible. El objetivo final es aumentar la temperatura del flujo de aire utilizado para la quema de combustible en hornos y otros procesos de calefacción, aguas arriba o aguas abajo del proceso productivo. En consecuencia, se logra una reducción del consumo de combustible fósil en los procesos convencionales de calentamiento. En este sentido, la aplicación del PCM-TES es una opción sostenible e innovadora para aumentar la eficiencia energética (5-10%) y reducir el impacto ambiental asociado.

En primer lugar, se desarrolló una investigación concienzuda de los posibles usos y aplicaciones de los PCM a alta temperatura para recuperar la energía de los hornos industriales y afrontar las implicaciones en la recuperación de calor residual, caracterizada por la alta variabilidad de los flujos y las temperaturas.

Por una parte, se llevó a cabo una evaluación detallada de los PCM y su aplicación en diferentes campos como en los sistemas de calentamiento industrial, la construcción, la climatización, la energía solar, el transporte, la refrigeración electrónica, la medicina, la conservación de alimentos y los procesos químicos. La idoneidad de los PCM se evaluó en el Capítulo 2 en función de sus propiedades termofísicas, pero también en términos de costo de los materiales, disponibilidad, peligrosidad y requisitos de las instalaciones. Además, durante dicha evaluación, se identificaron más de 500 PCM, listando sus propiedades más relevantes (temperatura de fusión frente al calor latente de la capacidad de fusión) y divididos en grupos según su composición química. En particular, se determinaron hasta 82 PCM como posibles alternativas para la aplicación a altas temperaturas (250-1000°C) y satisfacer el objetivo de la tesis. Entre los materiales más adecuados para trabajar a altos niveles de operación, destacan las sales hidratadas, carbonatos, cloruros y fluoruros. Como primera conclusión, se detectó una falta de materiales adecuados disponibles para altas temperaturas en comparación con los niveles de operación a media y baja temperatura.

La investigación de tecnologías TES alternativas en esta gama de altas temperaturas concluye que la tecnología basada en el calor latente presenta una eficiencia entre el 75 y el 90% para temperaturas de funcionamiento hasta 900-1000°C y su coste oscila entre 10 y 70 €/kWh. Por lo tanto, los sistemas de calor latente basados en el uso de PCM cumplen con el compromiso entre innovación y viabilidad tecnológica, lo cual les otorga gran potencial en un futuro a corto plazo.

Aunque existen algunos prototipos a escala de laboratorio; se ha comprobado que su aplicación en condiciones operativas reales es todavía limitada. La consolidación de esta tecnología a gran escala y en condiciones reales es una prioridad para su ulterior desarrollo y comercialización.

Por otra parte, la capacidad del material para almacenar y transferir calor depende en gran medida de las propiedades térmicas del PCM (calor latente, temperatura de fusión, calor específico, conductividad térmica, durabilidad y estabilidad cíclica). Se demostró que la observación y medición precisa de las propiedades térmicas de los PCM son fundamentales para cualquier proceso o material que experimente un gran cambio de temperatura y/o fase. Por consiguiente, en el Capítulo 3 se estudió la bibliografía de los equipos de caracterización y los métodos disponibles para medir las propiedades termofísicas de los PCM. En lo que respecta a la experimentación, se llegó a la conclusión de que la DSC es la técnica de análisis más empleada para estudiar los PCM, seguida de los análisis TGA, DTA y el método de T-History. En lo que respecta a la conductividad térmica, la técnica MTPS funciona correctamente para la mayoría de los PCM en un rango de - 50°C hasta incluso 500°C. Sin embargo, el método de LFA es más adecuado para la caracterización de PCM a altas temperaturas, como los metales y sus aleaciones.

En segundo lugar, la tesis pretendía diseñar, a nivel conceptual, una configuración de solución PCM-TES adaptada a las instalaciones y a las potenciales fuentes de calor de la planta.

El diseño original del sistema basado en PCM comienza desde el desarrollo conceptual, pasando por el diseño y la ingeniería básica, y finalmente, prepararlo para su integración en una planta industrial en condiciones reales de funcionamiento. La completa metodología aborda los aspectos técnicos e ingenieriles, y proporciona la flexibilidad suficiente para seleccionar un diseño totalmente adaptado al marco operativo de los sectores EII. Se eligieron dos casos de estudio (una planta industrial de producción cerámica y otra siderúrgica) representativos de algunos de los sectores consumidores de energía más intensivos, que presentan un gran potencial para la recuperación de calor. El calor residual de los gases de combustión a recuperar sale a altas temperaturas (750-1100°C) y los caudales oscilan entre 640 y 785 Nm^3/h. Estas características junto con las propiedades térmicas y físicas de los PCM fueron los parámetros clave para diseñar la configuración del equipo, teniendo en cuenta los requisitos para el sector cerámico y del acero.

Para lograr su aplicación satisfactoria a escala industrial, los PCM comerciales disponibles deben adaptarse a las necesidades de los usuarios finales (plantas y procesos). Se seleccionaron dos PCMs basados en sales inorgánicas como material de almacenamiento para ambos sectores y se caracterizaron experimentalmente en el Capítulo 3. En el caso de la industria siderúrgica, se consideró que el H500 era el PCM más apropiado para este sector, ya que las pruebas definieron su punto de fusión (509°C), mostró una alta capacidad de almacenamiento (260 kJ/kg) y manifestó ser seguro a temperaturas sobre 750-800°C. En el caso de la industria de cerámica, las pruebas realizadas con el H885 determinaron un calor latente alto (191 kJ/kg) y un punto de fusión deseable para la aplicación (888°C). Las pruebas de estabilidad y ciclabilidad revelaron que el material es estable en temperaturas inferiores a 950-1000°C y expuesto a una atmósfera de aire.

El diseño conceptual es el punto de partida para afrontar otros aspectos técnicos y de ingeniería para una implementación exitosa de la PCM-TES a nivel industrial. En el Capítulo 4 se propusieron cinco configuraciones alternativas de diseños conceptuales de PCM-TES, las cuales se evaluaron mediante trece criterios de decisión ponderando aspectos técnicos, económicos y de diseño. Para ello, se realizó un matriz para ayudar al la toma de decisiones mediante un ançaliss multi-criterio (MCDA), siguiendo una metodología de priorización jerárquica. Se destacaron con un valor positivo los aspectos favorables, considerando la adecuación a la aplicación, la flexibilidad del diseño y la adaptación de la configuración para lograr una solución técnica adecuada; mientras que se puntuaron con un valor negativo los inconvenientes cruciales o que suponen dificultades en el rendimiento/ensamblaje para descartar opciones técnica o económicamente inviables. La solución más adecuada resultó ser la configuración de carcasa y tubos (dobles concéntricos) integrando una capa de PCM entre ellos.

En tercer lugar, la ingeniería desarrollada en esta tesis tuvo como objetivo definir las dimensiones y la configuración geométrica del equipo de PCM-TES, de acuerdo con los diferentes requisitos de los procesos de cada sector.

En el Capítulo 5 se llevó a cabo la ingeniería mediante un proceso iterativo para ajustar la configuración del sistema, de acuerdo con los requisitos del proceso para cada sector específico. La tesis permitió determinar un conjunto de parámetros de diseño, como el diámetro y el número de tubos, el volumen del sistema, los materiales de construcción y los costes de equipo y materiales, para lograr un diseño PCM-TES consistente, eficiente y factible. Se utilizó un análisis de sensibilidad para determinar el número óptimo de tubos y el tamaño adecuado para cada solución, logrando un compromiso entre las perspectivas técnicas, prácticas y económicas. Estos resultados sirvieron de base para la documentación, los dibujos y los diagramas técnicos (hojas de especificaciones de la instrumentación, EPIs, disposición de la solución en la planta, etc.) en la búsqueda de un diseño PCM-TES con el fin de ser implementado a escala industrial.

El caso de estudio de la industria cerámica está diseñado para recuperar el calor residual de los gases de escape del horno, a niveles de temperatura muy altos (más de 1100°C). La energía almacenada sirve para precalentar la temperatura del aire de combustión que entra en el horno. El PCM-TES se instala en posición vertical para una mejor resistencia a la tensión mecánica y una limpieza y mantenimiento más fáciles. La configuración consiste en una carcasa externa que contiene tubos concéntricos de 2 m de largo y 600 mm de diámetro, llenos con 4700 kg de PCM. Los resultados obtenidos demuestraron la posibilidad de alcanzar niveles de temperatura muy elevados en el precalentamiento del aire de combustión (más de 700°C), corroborando así una mejora de la eficiencia energética y medioambiental, en comparación con los sistemas convencionales con salida de aire a 650°C. Según las pruebas de compatibilidad de materiales, en el sector cerámico se necesita una aleación a base de níquel porque presenta una resistencia a la fluencia y a la oxidación hasta 1200°C, que a cambio supone un elevado coste.

El caso de estudio en el sector del acero se basó en recuperar el calor residual a 800°C procedente de una antorcha de gas natural sintético, el cual proporciona la energía necesaria para cargar el sistema PCM durante los períodos en los que el gasificador quema el exceso de gas. En este caso, el número de tubos internos se fijó en 7, con 3 metros de largo y 270 mm de diámetro, mientras que el diámetro de la carcasa externa que contiene los tubos es de alrededor de 1.5 metros. Por cuestiones técnicas para la construcción y la transferencia térmica, el grosor del PCM se fijó en 35 mm. El material de construcción selecionado para el sector del acero es acero inoxidable 310S (con alto contenido de Cr), que resiste mucho mejor el ataque de la sal en comparación con el 316, y por lo tanto, es rentable y compatible con el PCM H500.

En cuarto lugar, otro objetivo importante era modelar el rendimiento térmico de la solución PCM-TES (ciclos de carga/descarga y los perfiles de temperatura) para seleccionar los materiales de construcción más adecuados.

Una vez definida la ingeniería para ambos casos, en el Capítulo 6 se desarrolló un modelo numérico en el software MATLAB® para investigar el rendimiento térmico (los perfiles de temperatura del PCM, los gases y el aire de combustión durante los procesos de carga y descarga). Se concluyó que tanto la convección como la conducción son fenómenos dominantes durante la fusión y solidificación del PCM. La convección natural es considerada en el modelo por medio de la conductividad efectiva, y es especialmente relevante durante la fusión dentro de los tubos concéntricos. Los resultados de la simulación permiten realizar un diseño adecuado ayudando en la selección de materiales de construcción y dimensionamiento, asegurando la viabilidad técnica de estos sistemas operando en rangos de temperatura críticos. Los resultados obtenidos demostraron la posibilidad de alcanzar altos niveles de temperatura en el precalentamiento del aire de combustión (de 700 a 865°C en el sector de la cerámica; de 300 a 480°C en el sector del acero). Adicionalmente, se evaluó la evolución de la carga y la descarga, resultando en ciclos largos (11 a 25 horas), donde la baja conductividad térmica del PCM influyó significativamente. Los resultados de la modelización numérica sirven, por un lado, como retroalimentación activa para los parámetros de diseño del PCM-TES, que pueden ajustarse en la función del modelo. Y por otra parte, el comportamiento térmico simulado constituye el primer paso de la validación del diseño del PCM-TES, facilita la selección de materiales a altas temperaturas y reduce el riesgo de incertidumbre en el rendimiento operativo y la integración in-situ a mayores escalas.

En quinto lugar, se desarrolló la documentación técnica y las especificaciones del prototipo PCM-TES estableciendo las condiciones de funcionamiento y el equipamiento necesarios para alcanzar los requisitos de fiabilidad, eficiencia y seguridad.

El desarrollo del Capítulo 7 permitió lograr una implementación del innovador prototipo industrial siguiendo las premisas del “Pensamiento de Diseño”, para generar ideas innovadoras que centran su eficacia en entender y dar solución a las necesidades reales de los usuarios. Para ello, se realizó una evaluación exhaustiva para adaptar y reajustar el sistema PCM-TES en función de los requisitos y las condiciones de operación de una planta industrial del sector siderúrgico. Como resultado, se redefinió la configuración del sistema, reduciendo el área total de transferencia de calor y el número de tubos (6 tubos en lugar de 7); de este modo, la masa de PCM (1400 kg de PCM) y la capacidad de almacenamiento del sistema disminuyeron, haciendo así pero ciclos de carga y descarga más rápidos. Se desarrolló una ingeniería más detallada para la creación del prototipo, a fin de proporcionar documentos técnicos, dibujos y especificaciones de los componentes; indicaciones sobre la ubicación del sistema PCM, el diagrama de proceso e instrumentación (PID), el equipo periférico y los suministros; la disposición del equipo, las conexiones y las necesidades de suministro para la integración del sistema a la planta; los procedimientos de montaje, desmontaje, mantenimiento, salud y seguridad y el procedimiento de llenado de los tubos concéntricos con PCM. Asimismo, se desarrollaron los procedimientos de funcionamiento (carga y descarga), se establecieron las condiciones de funcionamiento y la instrumentación del sistema de vigilancia y control para garantizar una solución lista para su validación. De este modo, la labor desarrollada contribuye a impulsar la integración de un sistema innovador, superando la actual carencia de conocimiento de aplicaciones de PCM-TES a nivel industrial, especialmente a altas temperaturas.

En sexto lugar, esta tesis planteó como objetivo proporcionar una validación prospectiva del modelo numérico del capítulo 6 y el diseño PCM-TES del capítulo 5.

Para ello, en el Capítulo 8, se compararon y desarrollaron dos enfoques de modelado numérico 3D para simular el comportamiento transitorio del sistema PCM-TES. Por un lado, el modelo simplificado propio de MATLAB® proporciona resultados suficientemente fiables y menor coste computacional; lo cual lo hace preferible durante las primeras etapas del diseño para su aplicación práctica en la ingeniería y la industria. Por otro lado, el enfoque del modelo COMSOL Multiphysics® es más preciso y versátil, ideal para simular problemas de multifísica; sin embargo, presenta un mayor tiempo de cálculo. Los resultados obtenidos permiteieron definir en detalle el rendimiento del sistema PCM-TES durante su operación. La corriente de aire de combustión recibió 338 kWh de calor liberado por parte del PCM durante las 3 horas de descarga, proporcionando una temperatura media del aire de combustión en el rango de 320-150ºC. Durante la carga, el PCM absorbió 351 kWh de la corriente de gases de combustión durante 6 horas. El ahorro de energía anual es de 230 MWh, considerando una duración de ciclo completo de 9 horas (carga + descarga) aplicado continuamente en el proceso de calentamiento de moldes de la planta del sector siderúrgico. Además, se evaluó la distribución de temperatura a lo largo de los tubos concéntricos de PCM, para asegurar que las condiciones de funcionamiento no superaban las temperaturas máximas de trabajo de los materiales de construcción seleccionados.

En séptimo lugar, otro objetivo específico era investigar la viabilidad y replicabilidad desde un enfoque intersectorial (sector cerámico, metalúrgico, químico, vidriero, cementero y papelero, entre otros) considerando aspectos técnicos y económicos.

La flexibilidad de los sistemas PCM ofrece la oportunidad de adaptar el diseño a los requisitos específicos de cada planta. En el Capítulo 9 se desarrolló una herramienta simplificada basada en el modelo MATLAB® como previabilidad del rendimiento y la integración PCM-TES en una planta industrial desde las perspectivas medioambiental, técnica y económica. En este sentido, la tesis evaluó, mediante un análisis paramétrico y de sensibilidad, el rendimiento tecno-económico de la solución PCM-TES bajo diferentes condiciones de trabajo y sectores de EII. Se estableció un conjunto de ecuaciones basadas en correlaciones entre los parámetros más relevantes del sistema PCM-TES como case de una herramienta de viabilidad. Como resultado, la conductividad térmica, el volumen y la capacidad de almacenamiento del PCM se erigieron como los parámetros más influyentes. Esta herramienta permite seleccionar dentro de una base de datos, un PCM adecuado para las condiciones de funcionamiento y así calcular el parámetros (masa y volumen del PCM, capacidad de almacenamiento, temperatura obtenida a la salida del sistema, ahorro de energía, coste económico) de la configuración de diseño del PCM-TES descrita en la tesis.

La selección del diseño, materiales y dimensiones adecuados son parámetros cruciales para obtener beneficios energéticos y económicos. Además, depende en gran medida de la velocidad de transferencia de calor y del tiempo en el que la energía debe ser almacenada o liberada, siempre de acuerdo con las condiciones de funcionamiento de la planta. Así pues, se llegó a la conclusión de que un PCM capaz de recuperar y transferir el calor más rápidamente aumentaría la adaptabilidad de integración del PCM-TES a una mayor variedad de procesos. Por lo tanto, en el Capítulo 9 se realizó una búsqueda de PCM entre los metales y sus aleaciones, para ser aplicables a altas temperaturas; aunque actualmente se desconoce su aplicación comercial y sus consecuencias desde el punto de vista metalúrgico (exceso de dilatación, pérdida o modificación de propiedades, maleabilidad, etc.). Como ejercicio comparativo, se evaluaron las aleaciones metálicas y las sales hidratadas inorgánicas mediante la herramienta de análisis multicriterio. Las sales inorgánicas presentaron un mayor ahorro económico y energético neto (26.400 euros; 480 MWh/año). Aunque los PCM metálicos son unas 10 veces más caros que las sales inorgánicas, se obtuvieron coeficientes de ahorro/inversión muy rentables, debido a su capacidad de almacenamiento y a la rapidez de carga y descarga. Sin embargo, el uso de metales implica mayores impactos en el indicador de cambio climático en comparación con las sales.

Por último, con el objetivo de evaluar su viabilidad técnica, se calculó el período de retorno del sistema PCM-TES para varios casos de estudio propuestos mediante un análisis paramétrico, cambiando el material PCM, el sector de operación y los parámetros de diseño.

En el sector cerámico, el funcionamiento del sistema a muy altas temperaturas se traduce en altos costes de equipo que dan lugar a períodos de retorno largos (más de 30 años). Este hecho manifiesta los obstáculos técnicos y económicos existentes a altas temperaturas. Mientras que, en el sector del acero, se observaron períodos de retorno mucho más aceptables (entre 5 y 8 años) con una eficiencia energética de alrededor del 10% durante la fase de descarga. Este dato conlleva hasta un 4% de ahorro anual para la planta industrial, dependiendo del PCM y del diseño final. Las grandes empresas de la industria de uso intensivo de energía tienen un elevado consumo de gas, lo que significaría un importante beneficio económico. Para conseguir mayores ratios de ahorro, se debería optimizar el diseño, el control de procesos y la integración en el sistema global. Además, el tiempo de amortización y los costes de inversión se reducirán considerablemente si el sistema PCM-TES se fabrica a escala comercial, y no como un único prototipo independiente.

En resumen, los resultados globales obtenidos a lo largo de esta tesis son un punto de partida para consolidar y promover sistemas basados en el PCM como soluciones tecnológicas y materiales innovadores, en lo que respecta a la investigación, la innovación y la viabilidad, para su aplicación a escala industrial. Esta línea de investigación está estrechamente alineada con los propósitos tanto de la comunidad científica como de la de ingeniería, por ejemplo en temática de desarraollo de materiales y diseños innovadores e inteligentes para optimizar el rendimiento de los sistemas de recuperación y almacenamiento de calor.

10.2 Trabajo futuro y próximas líneas de investigación

10.2.1 Innovación relativas a materiales

A continuación, se presentan recomendaciones para futuras investigaciones relativas a materiales PCM para el almacenamiento de energía térmica:

• Investigación de nuevos materiales que posean una alta conductividad térmica, como las aleaciones metálicas, en lugar de sales inorgánicas. El PCM metálico y sus aleaciones ofrecen, por un lado, una alta conductividad térmica y densidad de energía volumétrica, lo que implicaría un gran potencial para sistemas de carga más flexibles y rápidos. Aunque por otro lado, son más costosos y la integración en los sistemas es compleja debido a los problemas de expansión térmica y a las implicaciones de operar a altas temperaturas, lo que requeriría contenedores o revestimientos cerámicos para su encapsulado.

• Dado que la principal desventaja de los PCM es su baja conductividad térmica, que implica un largo tiempo para el cambio de fase; pueden emplearse estrategias de optimización para mejorar el ratio de transferencia de calor de los PCM. Futuras investigaciones incluirían la evaluación de la integración de los PCM incrustadas en espumas metálicas o estructuras malladas, así como otrs materiales innovadores, como los PCM microencapsulados o los nanomateriales.

• Selección de PCM con propiedades termofísicas mejoradas, probadas mediante la caracterización DSC y ensayados durante varios ciclos térmicos de fusión/solidificación para asegurar su rendimiento a largo plazo.

10.2.2 Mejoras de diseño del sistema

Asimismo, se pueden desarrollar nuevos estudios para complementar la labor realizada y avanzar más en los aspectos relativos al diseño del sistema y la simulación, como por ejemplo:

• Realizar un análisis paramétrico variando el número, longitud y tamaño de los tubos y el grosor de la capa PCM, para incrementar la transferencia de calor y aprovechar mejor el calor residual.

• Proponer nuevos diseños de la configuración del sistema PCM-TES para aumentar la eficiencia y mantener la temperatura de combustión del aire a un nivel constante. Por ejemplo, variando de la geometría del sistema, la localización del material PCM en tubos sólidos, la creación de diferentes rutas para las corrientes de fluidos de transferencia de calor, etc.

• Evaluar el efecto de las aletas verticales o radiales en la capa PCM por medio de simulaciones de modelos 3D, analizando la cantidad, la longitud y el grosor de las aletas, la disposición interna o externa, la temperatura de funcionamiento, el tamaño y los materiales de las aletas.

• Investigar otros fluidos de transferencia de calor con mayor conductividad térmica a la del aire, o integrando partículas como material de dopaje para aumentar sus propiedades. Sin embargo, los fluidos suelen verse restringidos por los requisitos de la planta y del proceso.

• Realizar una simulación dinámica del ciclo por lotes incluyendo tiempos de espera, para comprender cómo reaccionaría el PCM y estimar las pérdidas de calor en esos períodos.

10.2.3 Validación industrial

Una investigación experimental precisa permitiría estudiar el comportamiento y el rendimiento térmico del PCM-TES en condiciones operativas reales a escala industrial. Los resultados obtenidos en las simulaciones podrían compararse frente a datos experimentales adquiridos de una integración piloto del PCM-TES a fin de validar el sistema propuesto. Durante el desarrollo de la tesis, varias industrias de los sectores de la EII han mostrado gran interés en esta innovadora tecnología para la recuperación de calor residual en la comunidad industrial.

La retroalimentación de la herramienta con variables medidas directamente en las plantas de EII que integren sistemas PCM-TES permitiría mejorar la respuesta de la herramienta, obteniendo así resultados más precisos y fiables, replicables en más industrias y condiciones de producción. Para garantizar la robustez de la herramienta, en el futuro se deberían analizar los parámetros de los modos de funcionamiento del sistema PCM-TES integrado y trabajando bajo diferentes condiciones de operación (temperaturas de proceso, flujos, ciclos, volúmenes, etc.).

10.2.4 Sinergias

Finalmente, el trabajo futuro podría enfocarse en utilizar del calor recuperado por el sistema PCM-TES en procesos separados entre sí; de este modo, la eficiencia general de la planta también mejoraría. Unos sistemas de almacenamiento portátiles permitrían llevar la energía térmica desde el lugar donde se genera hasta el proceso que demanda calor. Es más, esta estrategia podría aplicarse no sólo dentro de la misma planta, sino también para extender su uso entre empresas, favoreciendo la simbiosis en los parques industriales.

«Insanity is doing the same thing over and over again and expecting different results»

Albert Einstein

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ANNEXES

In the following section, the Annexes belonging to the present thesis are gathered. Please note the numbering of the annexes list: the first number corresponds to the thesis chapter associated with it; and the second number corresponds to the order of appearance within it.

Annexe 1.1 – Article publications

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Carbon footprint of a thermal energy storage system using phase change materials for industrial energy recovery to reduce the fossil fuel consumption ☆

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HIGHLIGHTS

- TES system can increase energy efficiency while reducing carbon footprint.
- Waste heat recovery using PCM helps to reduce the heat production from fossil fuels.
- Environmental benefits, in terms of carbon footprint, are identified in this study.
- PCM with high latent heat value tend to achieve better results in the overall system.
- The KNO_3 manufacture entails higher carbon footprint values than other PCM analysed.

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ABSTRACT

Until now, a small number of studies have analysed the carbon footprint (CO_2 eq. emissions) of the application of Phase Change Materials (PCMs) in conventional Thermal Energy Storage (TES) systems considering different conventional fossil fuels as the source of heat. In those scarce studies, the different environmental impact categories were estimated using, on the one hand, diverse environmental methodologies and, on the other hand, different environmental evaluation methods (the midpoint and endpoint approaches). Despite the fact that several researchers have used the Life Cycle Assessment (LCA) methodology as a tool to estimate the environmental impact of TES systems, there is no unanimity in the scientific community on the environmental evaluation method to be used. As a consequence, research results cannot be easily compared. This article evaluates the introduction of a TES system (using different PCMs) to recover the waste thermal energy released in industrial processes, which can be used in other applications, thereby avoiding fossil fuel consumption by the associated equipment to produce thermal energy. Five different fossil fuels have been considered to generate the 20 case studies that were analysed using the same methodology (LCA) and evaluation method (Global Warming Potential, GWP100, a midpoint approach). The results were used to identify the best cases, considering the environmental benefits that they generate. Additionally, this research indicates that the benefits can be achieved since, in general, the amount of conventional fuels saved is sufficiently large to balance the environmental impact associated with the inclusion of PCMs in conventional TES. Nevertheless, the selection of a PCM can increase or eliminate the environmental benefits obtained.

1. Introduction

Currently, large amounts of thermal energy are lost every day in the industrial sector, especially in processes running at medium or high temperatures. Sensible Thermal Energy Storage (TES) systems are an interesting alternative to manage that lost energy, such as Miró et al. [1] showed in the development of an experimental characterisation of a solid industrial by-product as material for high temperature sensible TES. However, Latent Heat Storage (LHS) systems have emerged as an attractive option. This is evidenced in the Oró et al. [2] which is focused on numerical comparing of two packed bed storage with Phase Change Materials (PCMs). On the other hand, at experimental level, some advances were

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Integration of environmental indicators in the optimization of industrial energy management using phase change materials

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A B S T R A C T

This work addresses the potential environmental effects of thermal energy storage using the life cycle assessment to perform an optimal system framework. The study assesses the recovery of waste thermal energy at medium temperatures through the application of phase change materials and the recovered heat use in other industrial processes avoiding the heat production from fossil fuel. To this end, twenty different situations were analysed in terms of energy and environmentally combining four thermal energy storage systems varying the type of phase change material incorporated (potassium nitrate, potassium hydroxide, potassium carbonate/sodium carbonate/lithium carbonate and lithium hydroxide/potassium hydroxide) which were defined as cases and five scenarios were the heat can be released based on the type of fossil fuel consumed (coal, heavy fuel, light fuel, lignite and natural gas). Moreover, a net zero environmental metric time parameter was calculated to assess the time period in which the environmental impacts associated to the thermal energy system were equal to the avoided impacts by the use of the heat recovered. Values that were lower than the thermal energy system lifetime were obtained in more than 40% of the total study situations. Finally, an additional analysis was performed to identify the most significant parameters for the further development of a mathematical model to predict the net zero environmental metric time.

1. Introduction

There are a large number of industrial processes in which thermal energy is lost every day, especially those processes running at low and medium temperatures. In addition to the reduction in the amount of excess energy released by production processes, several options are available for the use of industrial excess energy, including heat harvesting, heat storage, heat utilization and heat conversion technologies [1]. This energy is commonly called waste heat, and its optimal use represents a significant opportunity to establish advanced Thermal Energy Storage (TES) technologies [2]. As studied by different models [3], TES can store waste heat and then release it to different industrial applications [4]. Concretely, Kere et al. [5] studied the applicability of a TES system in the ceramic sector. Thereby, the consumption of other energy resources for heat production is avoided [6].

Previous studies have focused on advanced TES development using Phase Change Materials (PCMs) [7], which are able to use their latent heat as a way to store heat. In this sense, Fernandes et al. [8] developed a comparison of different possibilities available for energy storage and specially for high temperature thermal energy storage they highlighted the suitability of metal foams as PCM to improve the metal thermo-mechanical properties.

The heat storage is a capacity very useful, especially regarding those systems which involve heat exchange [9], so different techniques are been analysed in order to improve the heat transfer. One option is the use of fins inside the thermal management systems, as is was used reported by Al-Abidi et al. [10] containing sixty panels divided into nine internal horizontal fins acting as a heat exchanger. On the other hand, there are other methods that enhance the heat transfer by means of tubes as was reported by Tay et al. [11] who studied experimentally a TES system based on tubes inside a PCM filled cylindrical tank. By properly selecting the PCM, this technology can be used in the temperature range of 300–400 °C [12]. $NaNO_3$ is a typical inorganic salt example used in the mentioned above temperature range [13] and even a combination of a deformable copper shell filled with a nitrate mix of KNO_3–$NaNO_3$ can be used as example of encapsulated PCM [14]. Although required materials for encapsulation (refractory steel, extruded ceramics) are recognised to be expensive [15], their long lifetime upon charging–discharging cycles reduces the financial impact.

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Hybrid diagnosis to characterise the energy and environmental enhancement of photovoltaic modules using smart materials

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ABSTRACT

Growing demands for energy, gradual depletion of fossil resources and high environmental impacts require that current energy production models be replaced by more sustainable technology. Thus, research efforts focused on improving energy efficiency and material efficiency are considered extremely relevant.

In the following work, the influence of incorporating PCMs (phase change materials) on electricity conversion efficiency discussed along with hot spot prevention and lifetime increases in BIPV (building-integrated photovoltaics). The main goal is to evaluate the operational temperature control in a BIPV with or without PCMs considering different climatic severities. A design parameter analysis was conducted, and the importance of suitable PCMs and proper system designs are revealed. Also, this study indicates that areas with different climatic severities must be considered for widespread evaluations of this technology application to impact diverse regions.

Additionally, an environmental analysis based on the LCA (life cycle assessment) methodology was performed using the SimaPro software. The results show that a positive environmental impact is generated by PCM applications because of the decreased amount of consumed resources in BIPV manufacturing, which is related to the lifetime extension resulting from the ability of PCMs to store latent heat and prevent premature physical damage to the BIPV.

1. Introduction

In recent years, the demand for energy has significantly increased because of use in sectors such as industry, transportation, construction, and electric generation and as a result of an increased quality of life in many countries. Thus, consumerism and population growth have led to an increasing demand for natural resources and raw materials [1,2]. For years, fossil fuels and nuclear energy have been dominant sources of energy [3]. However, the production of these fuels results in the depletion of fossil resources and leads to significant environmental impacts. Therefore, the current model of energy production must be substituted for a more sustainable model to reduce energy and material consumption.

In the near future, renewable energy should have increased importance [4]. Among such energies, solar energy has become a promising option in many countries [2]. The earth's surface receives an average solar irradiance that is thousands of times higher than the global energy demand. This solar energy can be transformed into electricity using PV (photovoltaic) cells, or it can be utilised as thermal energy through the use of collectors [5]. The EPIA (European Photovoltaic Industry Association), in collaboration with Greenpeace, reported an annual growth in worldwide PV power generation of approximately 40% from 2000 to 2010 [6]. A second publication, InterSolar and EPIA [7] reveals that the production from installed worldwide PV cells amounted to almost 140 GW in 2013. Moreover, this figure is predicted to grow to 345 GW by 2020 and 1100 GW by 2030.

Current designs have non-technological and technical limitations, such as the high cost of installation and distribution. Technical limitations affect the lifetime, electrical production and energetic and environmental efficiency of PV cells [8,9]. At present, the electric conversion efficiency of cells is low, between 15 and 17% on average [10]. Another problem that affects the adoption of PV cells is local overheating, which is known as a hot spot. This phenomenon occurs when the current exceeds the module's short-

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Retrofitting strategies for improving the energy and environmental efficiency in industrial furnaces: A case study in the aluminium sector

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ABSTRACT

This study aims to analyse some of the most relevant issues that the energy intensive industry needs to face in order to improve its energy and environmental performance based on innovative retrofitting strategies. To this end, a case study based on the aluminium industry, as one of the most relevant within the European energy intensive industry has been thoroughly discussed. In particular, great efforts must be addressed to reduce its environmental impact; specifically focusing on the main stages concerning the manufacturing of an aluminium billet, namely alloy production, heating, extrusion and finishing. Hence, an innovative DC (direct current) induction technology with an expected 50% energy efficiency increase is used for retrofitting conventional techniques traditionally based on natural gas and AC (alternating current) induction. A life cycle assessment was applied to analyse three different scenarios within four representative European electricity mixes. The results reported reductions up to 8% of Green House Gases emissions in every country. France presented the best-case scenario applying only DC induction; unlike Greece, which showed around 150% increment. However, the suitability of the new DC induction technology depends on the electricity mix, the technological scenario and the environmental impact indicators. Finally, environmental external costs were assessed with comparison purposes to evaluate the increase of energy and environmental efficiency in existing preheating and melting industrial furnaces currently fed with natural gas.

1. Introduction

Energy intensive industries, including sectors such as che7micals, steel, aluminium, cement, ceramics and paper, are responsible for great environmental, economic and social impacts. About 3% of world's total energy is used in industrial sectors and the world power demand represented around 60 billion MW in 2015 [1]. Unfortunately, there is usually strong overlap of interest for energy-intensive industries and climate change goals [2]. Many efforts are focused on decarbonising the manufacturing industry by means of key actions such as fuel switching to less carbon intensive fuels, carbon capture and storage and alteration of the product design taking into account the lifecycle of the product [3]. So they are continuously facing new challenges in order to increase the efficiency, reliability and flexibility of their processes. However these changes disrupt the production or require sometimes high investment or an in-depth renovation process [4]; thus retrofitting strategies arise as promising and more cost-efficient actions in industrial plants. Most notably, industrial furnaces have been the focus of multiple researches as one of the most energy intensive processes [5], representing more than 40% of the energy consumption in European industry sector [6].

The main goals of retrofitting strategies are focused on addressing radical improvements in the competitiveness and energy, environmental and cost performance, which can be implemented at component, process, system, and organizational level [7]. To that end, the development of improved designs based on new materials and/or technologies, alternative feedstocks, equipment and the integration of permanent monitoring and control systems into new and existing furnaces seem to be essential instrument to meet the demands. A retrofitting action should be carefully weighed against the benefits and costs of new

Abbreviations: A, Acidification; AC, Alternating current; AD, Abiotic depletion; ADF, Abiotic depletion (of fossil fuels); Al, Aluminium; CO_2 eq., Equivalent carbon dioxide emissions; DC, Direct current; E, Eutrophication; EC, External costs; ECF, External cost conversion factor; EI, Environmental impact indicator; FWE, Fresh water aquatic ecotoxicity; FR, France; GHG, Greenhouse gases; GR, Greece; GWP 100a, Global warming (100 years); HT, Human toxicity; IT, Italy; LCA, Life Cycle Assessment; LCC, Life Cycle Costs; LCI, Life Cycle Inventory; MAE, Marine aquatic ecotoxicity; NG, Natural Gas; ODP, Ozone layer depletion; PO, Photochemical oxidation; S, Scenario; SP, Spain; TE, Terrestrial ecotoxicity

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High-temperature PCM-based thermal energy storage for industrial furnaces installed in energy-intensive industries

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A B S T R A C T

The energy considered as waste heat in industrial furnaces owing to inefficiencies represents a substantial opportunity for recovery by means of thermal energy storage (TES) implementation. Although conventional systems based on sensible heat are used extensively, these systems involve technical limitations. Latent heat storage based on phase change materials (PCMs) results in a promising alternative for storing and recovering waste heat. Within this scope, the proposed PCM-TES allows for demonstrating its implementation feasibility in energy-intensive industries at high temperature range. The stored energy is meant to preheat the air temperature entering the furnace by using a PCM whose melting point is 885 °C. In this sense, a heat transfer model simulation is established to determine an appropriate design based on mass and energy conservation equations. The thermal performance is analysed for the melting and solidification processes, the phase transition and its influence on heat transference. Moreover, the temperature profile is illustrated for the PCM and combustion air stream. The obtained results prove the achievability of very high temperature levels (from 700 to 865 °C) in the combustion air preheating in a ceramic furnace; so corroborating an energy and environmental efficiency enhancement, compared to the initial condition presenting an air outlet at 650 °C.

1. Introduction

Over the past century, awareness of the environmental sustainability principle has been increasing worldwide and has become deeply rooting in the culture of companies and industries. At present, numerous compromises and initiatives aim at boosting the key performance guidelines in order to meet environmental targets [1]. In particular, the energy-intensive industry (EII), which is composed of aluminium, cement, steel, ceramic, glass and chemical industries, among others, is making significant efforts to decarbonise their sectors following the 2050 roadmap for energy [2], while being economically competitive. However, it is not straightforward to achieve an industrial sector with zero carbon dioxide emissions and strong commitment is required in order to construct a plan for a low carbon society. EII is facing major challenges to avoid dangerous anthropogenic interference with the climate system; for example, by achieving the global warming target of 'well under 2° Celsius' expressed in the Paris Agreement [3]. To this end, the key actions are focused on implementing clean energy policies, renewable energy integration, switching to alternative fuels, removing carbon dioxide from the atmosphere by means of sequestration, developing advanced materials, integrating energy storage and adopting the superior available technologies [4,5], all under a lifecycle product approach. All of these strategies arise as promising actions to improve energy and resources efficiency, optimise production processes, reduce heat losses and minimise residues [6]. In particular, the integration of energy transformation and recovery is emphasised in order to avoid unnecessary entropy production, while causing the production processes to be more cost-effective and environmentally friendly [7]. This concept approach of integration, flexibility and symbiosis is defined as Smart Energy System, according to H. Lund et al. [8].

The industrial sector accounts for one third of the total energy consumed in society, of which a substantial part eventually becomes waste heat owing to inefficiencies. The average thermal efficiency for installed industrial furnaces is approximately 60% [9],

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Multiple-Criteria Decision Analysis and characterisation of phase change materials for waste heat recovery at high temperature for sustainable energy-intensive industry

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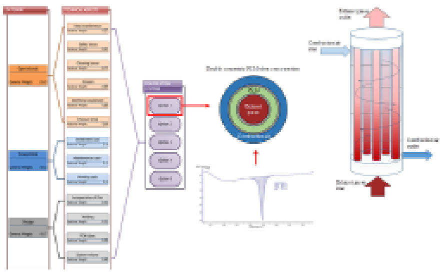
HIGHLIGHTS

- A phase-change material system is proposed working at high temperature for waste heat recovery.
- Thermal characterisation and cycling were conducted on the candidate storage material.
- Two phase change materials are identified for the application with a high latent heat capacity and thermal stability.
- A multiple-criteria decision analysis defined shell and double concentric tubes storage as the most suitable configuration.

GRAPHICAL ABSTRACT



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ABSTRACT

A latent heat storage system based on Phase Change Materials (PCMs) is proposed to increase the energy and environmental efficiency by recovering and storing waste heat from combustion gases or other surplus sources at in the energy-intensive industries (EII), currently unused. The final configuration design is specifically adapted to the plant operational requirements, by means of a methodology combining the search of the best conceptual design and a proper selection of core PCMs. To that end, a selection of suitable PCM is carried out by using characterisation techniques and thermal stability testing. Furthermore, relevant key factors are weighted by an in-house Multiple-Criteria Decision Analysis (MCDA) to define the most promising design options to be implemented in two plants belonging to the EII sector. For the ceramic sector, the design resulted in a shell-and-tube system with 1188 kg of a PCM melting at 885 °C and encapsulated in double concentric tubes, involving a storage capacity of 227 MJ. Similarly, 1606 kg of PCM, whose phase-change temperature is 509 °C, is selected for the steel sector providing a PCM-TES system capable to store 420 MJ.

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Thermal performance investigation on latent heat thermal storage for waste heat recovery from a high temperature gas flow in energy-intensive industries

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An important amount of high grade energy (>300°C) used in industrial activities is lost every day through production process outputs, such as the final product, by-products or emitted gases; with special relevance in the energy-intensive industry (EII). Several options are available for the re-use and recovery of industrial waste energy, including thermal energy harvesting, utilization, conversion and storage technolgies. The recovery of unused waste heat by means of advanced thermal energy storage (TES) technologies has an immense potential to save primary energy and resources and to reduce the environmental impact. Nonetheless, little attention has been paid for TES integration at EII applications up to now, since only about 5% of the final energy consumption is recovered. Even though conventional systems based on sensible heat are used extensively, technical limitations prevent them from achieving the maximum efficiency. Latent heat TES systems based on phase-change materials (PCMs) is a promising alternative to reduce size, operational failures and manufacturing and operating costs of conventional recovery systems. TES systems work on a cyclic process involving a charging phase, then the storage of the energy, and finally the heat discharging on-site or off-site. At present, there is a wide number of lab-scale prototypes and experimental pilot plants; however, implementation under real operational conditions are an unavoidable priority to achieve a large-scale practical use and commercialization. This shortage is even more highlighted at high temperature levels due to cost-effectiveness, thermal stability, compatibility and corrosion issues. In short, more efforts are needed to boost PCM-based latent heat TES technology and this is the main motivation of the current work.

To this end, an innovative and advanced PCM-TES is proposed to store waste heat by means of the PCM latent heat capacity; then, the stored energy is released by a phase change in the material to increase the combustion air temperature. This smart use of the recovered heat contributes to improve the energy and environmental efficiency of new and existing EII furnaces. A 3D heat transfer numerical model is used to assess the thermal performance (charge/discharge and temperature profile), ease the material selection (shell, tubes, insulation), and set the sizing specifications under the operational conditions of each industrial demosite. The flexibility of the PCM systems allows adapting the designs depending on the specific plant requirements, what increase their replicability. PCMs with different thermo-physical properties are analysed based on the influence observed in the thermal performance. Specifically, key parameters of PCM-TES process integration are reported for two different EII sectors (ceramic and steel), showing its performance in both continuous and batch production processes. The recovered heat from high temperature exhaust gases (800-1100 °C) is used to preheat the combustion air stream entering the furnace, where up to a 200-degree temperature increase is achieved. Consequently, this increase leads to primary energy savings (up to 12%). In conclusion, the design and engineering results are a starting point in the consolidation and validation of new smart materials integrated in innovative technologies at industrial scale towards industry 4.0.

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COMPUTER-AIDED DESIGN FOR HIGH TEMPERATURE PCM-BASED TES WORKING WITH COMBUSTION EXHAUST GAS FLOW OF INDUSTRIAL FURNACES INSTALLED IN THE ENERGY INTENSIVE INDUSTRIES

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Keywords: Phase Change Materials (PCM); high temperature thermal energy storage (TES); Intensive Energy Industries; Furnace efficiency; heat transfer- simulation model

Abstract

Intensive industries are continuously facing new challenges in order to increase efficiency and reliability of their production processes. In particular, industrial furnaces are under the spotlight of multiple researches, since they are one of the most energy intensive processes. One of the key actions to improve the overall performance of industrial furnaces is the implementation of energy recovery solutions. In this sense, combustion furnaces have important heat losses in flue gases. However, much of this heat can be recovered and re-used to increase the thermal efficiency not only of the furnace but also of the whole system. Although conventional energy recovery systems are broadly used, some technical limitations hinder the achievement of maximum efficiency. Latent Heat Storage systems based on phase change materials (PCM) have emerged as an innovative and alternative option to establish advanced Thermal Energy Storage (TES) technologies. Compared to conventional sensible heat based systems, which are simple and less expensive, but require large amount of storage material and valuable space; PCM-TES systems can provide a much high-energy storage density and then release it to different industrial applications with an nearly isothermal behaviour during the phase change. The integration of PCM would allow reducing the energy resources consumption, environmental impact and operating costs of the industrial systems unable to manage the waste energy generated. However, the applications and studies found at high temperature levels is very limited due to technological and economic barriers. Under this scope, this study aims to demonstrate the feasibility of implementing a PCM-based TES to recover the wasted energy at high temperature from melting furnaces of the energy intensive industry. To this end, a two-dimensional heat transfer model is performed to find a suitable design. The model allows carrying out simulations of charge/discharge cycles to study the PCM thermal behaviour and is highly adaptable to the key parameters of the system design.

1

INFUB-12 Porto, Portugal, 14th-17th April 2020

Novel heat recovery system for ceramic furnaces using high-temperature phase change materials and integration based on multicriteria analysis development

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Abstract

Waste heat recovery is one of the solutions included in the roadmap for reducing both energy consumption and the carbon footprint. Its high replication capacity in steel, ceramics, pulp and paper, and other energy-intensive industries favours the efficiency of the process and, consequently, achieves reductions in consumption, pollution and the equipment size and cost. As a result, the large-scale deployment of those innovative technologies is determinant for achieving energy efficiency and climate changes objectives in an effective and efficient manner. In this vein, VULKANO and RETROFEED projects implements and validates an advanced retrofitting solution to improve the overall efficiency and reduce emission in intensive sectors. On this route, a novel high-temperature Phase Change Materials (PCMs)-based thermal energy storage system (TES) for industrial furnaces is evaluated to increase the energy and environmental efficiency by recovering waste heat from the combustion gases. Design details such as preliminary sizing, costs and conceptual design configuration is presented as an example of integration at industrial scale, adapted to the plant operational requirements, by searching the best conceptual design and a proper selection of core materials. A multicriteria analysis is developed and applied to select the most profitable system configuration. The methodology is based on technical indicators, that is, life cycle assessment, life cycle cost, and techno-economic analysis, to assess both the status quo of existing gas furnaces and their modification after incorporating the PCM-TES. The potential for improving efficiency, reducing environmental impact and cost savings is determined by implementing the waste heat recovery system. Consequently, this methodology considers and integrates the analysis of horizontal and vertical value chain that can be used as a prefeasibility analysis based on a decision support tool for defining reproducibility and replicability.

Keywords

High temperature thermal energy storage, waste heat recovery, phase change materials, energy-intensive industry, multicriteria analysis, system integration.

Nueva generación de placas fotovoltaicas

Evaluación técnica

Aplicación de materiales avanzados para optimizar su eficiencia

Patricia Royo, Víctor J. Ferreira, Ana M. López-Sabirón, Germán Ferreira

La creciente demanda de energía, el agotamiento gradual de los recursos fósiles más accesibles y los altos impactos ambientales que generan los modelos de producción de energía actual requieren que sean sustituidos por una tecnología más sostenible. Por lo tanto, es en esta dirección donde deben centrarse los esfuerzos de investigación, especialmente orientados a aumentar la mejora de la eficiencia energética y la eficiencia en el consumo de materiales para los nuevos modelos de producción.

Actualmente, en edificación, las placas fotovoltaicas integradas en edificios (BIPV según sus siglas en inglés, Building Integrated Photovoltaic) juegan un papel cada vez más relevante en el aprovechamiento de la Energía Solar. Sin embargo, los actuales diseños poseen ciertas limitaciones técnicas que reducen su eficiencia durante la operación. Una de las alternativas más prometedoras para la reducción de los consumos energéticos y materiales asociados a las BIPV es la incorporación de Materiales de Cambio de Fase (PCM según sus siglas en inglés, Phase Change Materials), capaces de almacenar y ceder energía térmica en un rango determinado de temperatura.

Esta innovadora tecnología, basada en materiales inteligentes, permite aumentar la eficiencia de las BIPV. A su vez, esta tecnología permite prolongar la vida de la BIPV, pues la aplicación de los PCM puede evitar la degradación prematura de la instalación.

Esto conlleva una reducción en el impacto ambiental de ciclo de vida de las placas fotovoltaicas al evitar la reposición de los materiales degradados en tiempos más breves.

Esta investigación propone una evaluación técnica para caracterizar el comportamiento de distintas variables en la operación BIPV, con o sin aplicación PCM, las cuales son factores clave para la prevención de puntos calientes y por tanto, para el aumento de la eficiencia de conversión eléctrica y el tiempo de vida útil de las BIPV.

SOLAR FOTOVOLTAICA

Lo que los **materiales inteligentes** pueden aportar

La integración de materiales inteligentes en placas fotovoltaicas puede aumentar la eficiencia ambiental y energética de los diseños convencionales. Así lo cree el equipo de investigadores del Centro de Investigación de Recursos y Consumos Energéticos (Circe) que firma este artículo.

Patricia Royo, Ana M. López-Sabirón, Víctor J. Ferreira y Germán Ferreira*

El informe *Global Market Outlook for Photovoltaics 2014-2018*, publicado por InterSolar y la Asociación Europea de la Industria Fotovoltaica (EPIA) en junio de 2014, estima que en 2020 pueden alcanzarse los 350 GW de potencia fotovoltaica instalada en el mundo. Y prevé un constante aumento a medio plazo. Aumento que también está relacionado con el desarrollo de tecnologías innovadoras para producir FV de nueva generación (Figura 1).

No obstante, a pesar de las nuevas aplicaciones y crecientes tendencias en la producción, las instalaciones FV todavía tienen una baja participación en la generación mundial de electricidad: únicamente un 1,8%. Por tanto, deben promoverse diseños de instalaciones que optimicen el funcionamiento del sistema y que reduzcan el consumo de materiales, para así poder disminuir los impactos ambientales asociados. En este sentido, la incorporación en paneles fotovoltaicos de materiales de cambio de fase, llamados comúnmente PCM por sus siglas en inglés, persigue fomentar el aprovechamiento de la energía solar y romper barreras tecnológicas, incrementar la eficiencia ambiental y energética, disminuir el deterioro de los módulos e impulsar las energías renovables.

Reguladores de temperatura y almacenamiento de calor

Los paneles FV más comercializados tienen una eficiencia de conversión eléctrica (ηpv) aún demasiado baja, alrededor del 16%. Otro aspecto crucial a destacar en el funcionamiento óptimo de estos sistemas es su vida útil (aproximadamente 25 años), es decir, el período de tiempo en el cual garantiza como mínimo el 80% de su potencia nominal. El factor fundamental común a los mecanismos de degradación prematura son las altas temperaturas de operación (Tpv), ya que aceleran los procesos físicos de corrosión y decoloración. A mediodía, cuando la presencia del sol incide con más fuerza, la temperatura de operación llega a alcanzar valores tan altos (de hasta 80º C) que ponen en peligro la integridad de los materiales y el funcionamiento de la instalación fotovoltaica.

Para lograr que la tecnología FV sea considerada como una de las bases energéticas es necesario aumentar el porcentaje de conversión de energía solar a electricidad y disminuir las pérdidas de calor. Y la utilización de PCM puede ser una herramienta con mucho potencial.

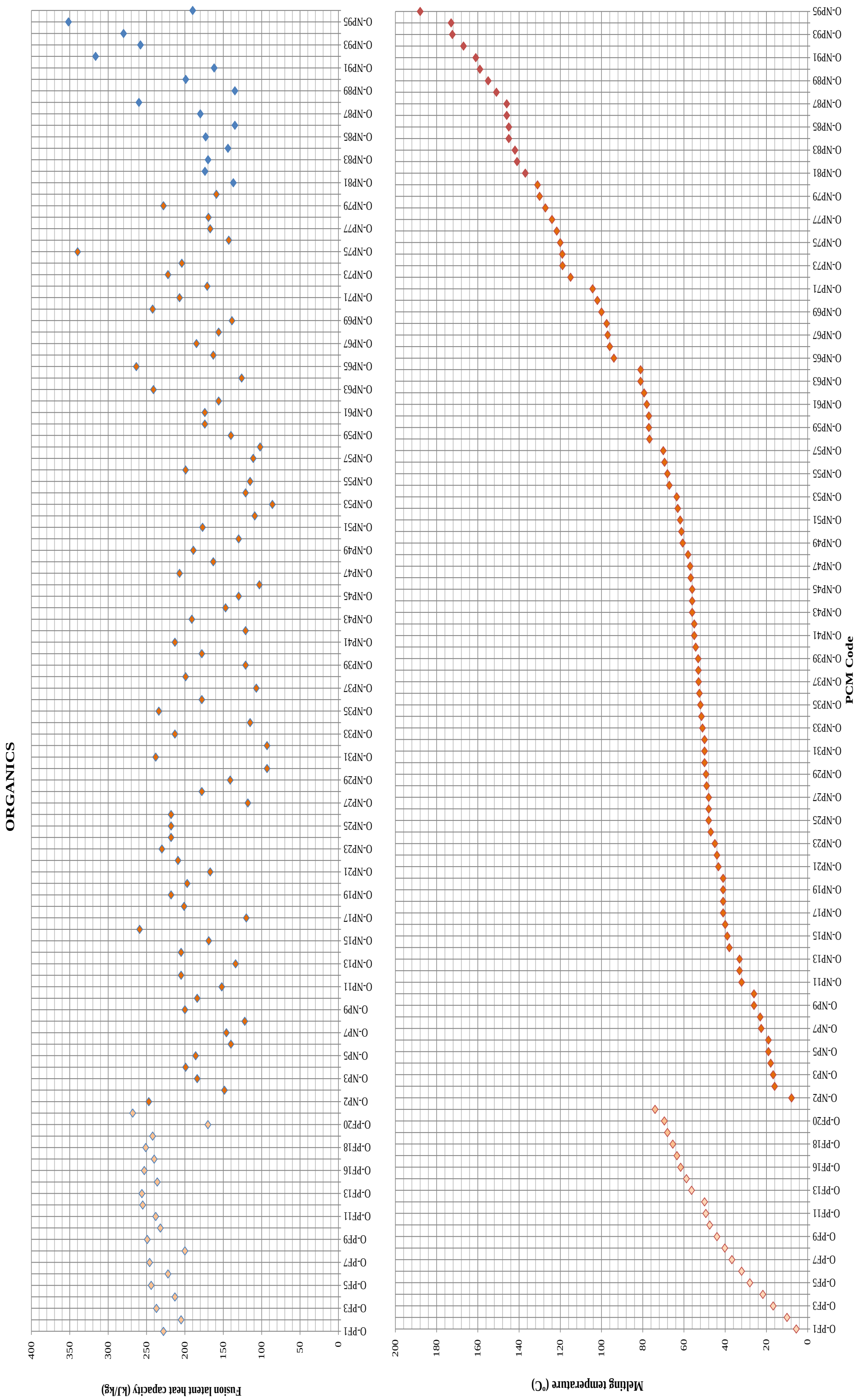
Un PCM es cualquier sustancia o compuesto que cambie de fase, ya sea de sólido a líquido, de líquido a gas o viceversa. Estos materiales son considerados pasivos e inteligentes, ya que al llegar a su temperatura de cambio de fase (Tfusion), absorben o liberan energía en forma de calor latente manteniendo su temperatura constante y favoreciendo la transferencia de calor. Por otro lado, el calor latente de fusión es mucho mayor que el calor sensible, y por tanto aumenta notablemente la capacidad de almacenamiento.

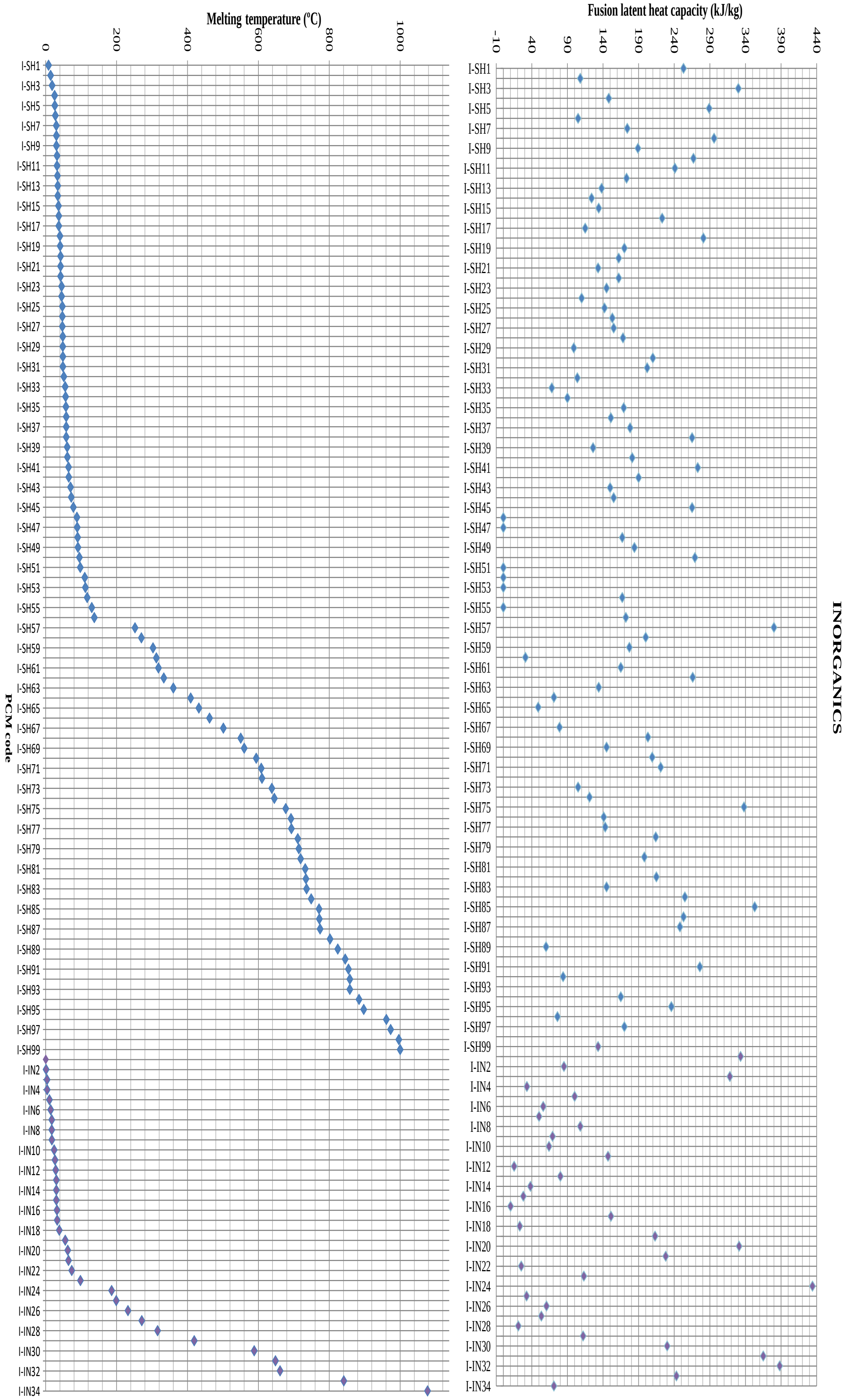
Prácticamente cualquier material puede considerarse un PCM, pero existen notorias diferencias entre sus propiedades termofísicas debido a su naturaleza. Es por eso que la clasifica-

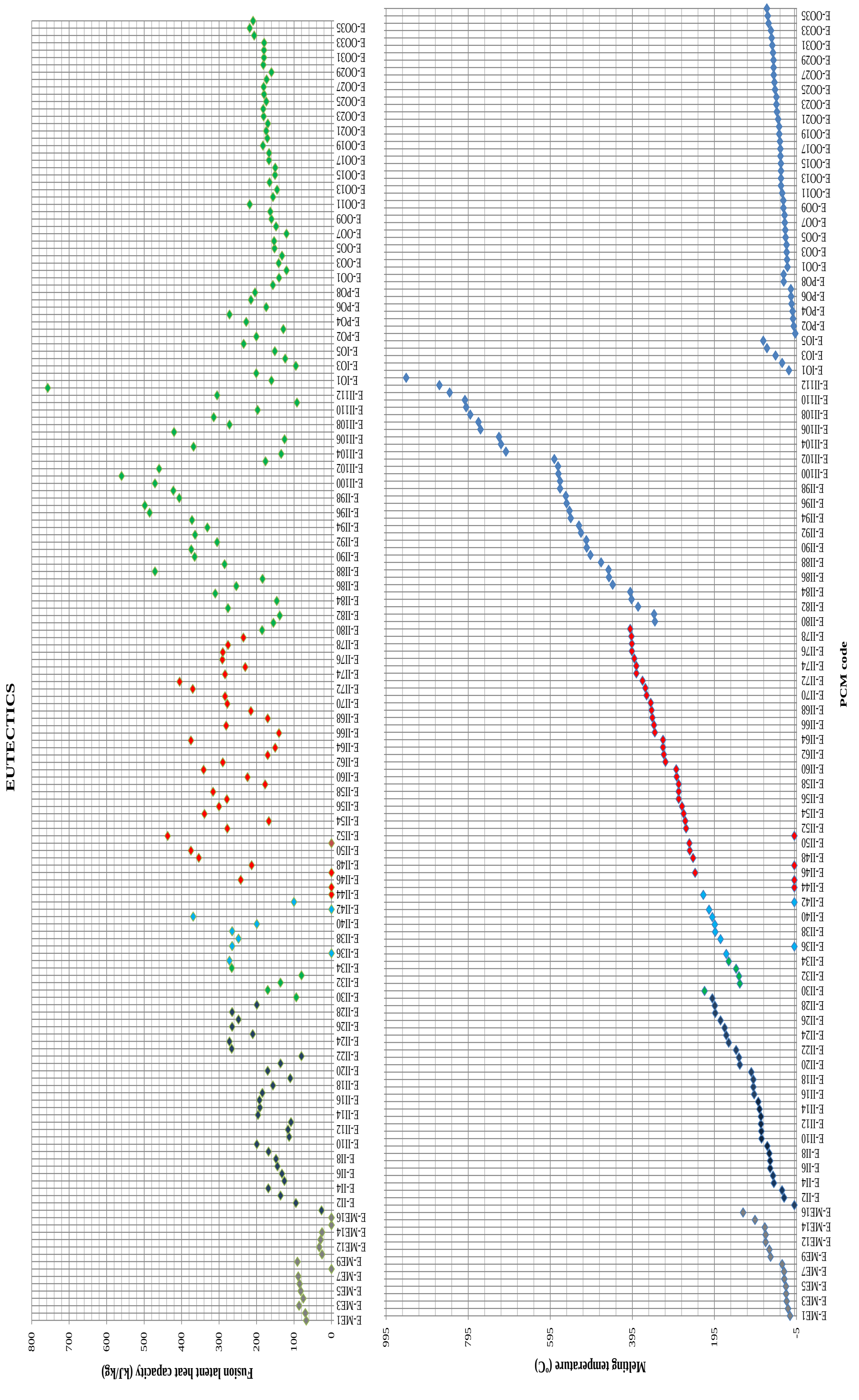
Figura 1. Fundamentos y bases para el aumento del aprovechamiento de la energía solar fotovoltaica

Figura 2. Clasificación de los PCM según su composición química

Annexe 2.1 – Review of PCMs, lists and mapping




Melting temperature (°C)
0
200
400
600
800
1000
Fusion latent heat capacity (kJ/kg)
-10
40
90
140
190
240
290
340
390
440
PCM code
INORGANICS


EUTECTICS
Fusion latent heat capacity (kJ/kg)
Melting temperature (°C)
PCM code

Organics	**PCM**	**Code**
PARAFFIN	n - Tetradecane	O-PF1
	n - Pentadecane	O-PF2
	n - Hexadecane	O-PF3
	n - Heptadecane	O-PF4
	n - Octadecane	O-PF5
	n - Nonadecane	O-PF6
	n - Eicosane	O-PF7
	n - Heneicosane	O-PF8
	n - Docosane	O-PF9
	n - Tricosane	O-PF10
	n - Pentacosane	O-PF11
	n - Tetracosane	O-PF12
	n - Hexacosane	O-PF13
	n - Heptacosane	O-PF14
	n - Octacosane	O-PF16
	n - Nonacosane	O-PF17
	n - Triacontane	O-PF18
	n - Hentriacontane	O-PF19
	n - Dotricontane	O-PF20
	n - Tritricontane	O-PF21
NON PARAFFIN	Formic acid	O-NP2
	Caprylic acid	O-NP1
	Acetic acid	O-NP3
	Glycerin	O-NP4
	Propyl palmitate	O-NP5
	Butyl stearate	O-NP6
	Polyethylene glycol 599	O-NP7
	Ethyl palmitate	O-NP8
	1-dodecano	O-NP9
	d-Lattic acid	O-NP10
	Capric acid	O-NP11
	Methyl palmitate	O-NP12
	Ethyl stearate	O-NP13
	1-tetradecanol	O-NP14
	Methyl stearate	O-NP15
	Caprylone	O-NP16
	Phenol	O-NP17
	Heptadecanone	O-NP18
	1-Cyclohexylooctadecane	O-NP19
	4-Heptadacanone	O-NP20
	p-Toluidine	O-NP21
	Cyanamide	O-NP22
	Methyl isocyanate	O-NP23
	Elaidic acid	O-NP24
	3-Heptadecanone	O-NP25
	2-Heptadecanone	O-NP26
	Hydrocinnamic acid	O-NP27
	Lauric acid	O-NP28
	Cetyl alcohol	O-NP29
	α-Nepthylamine	O-NP30
	Camphene	O-NP31
	O-Nitroaniline	O-NP32
	9-Heptadecanone	O-NP33
	Thymol	O-NP34
	Methyl behenate	O-NP35
	Pentadecanoic acid	O-NP36
	Diphenyl amine	O-NP37
	Myristic acid	O-NP38
	p-Dichlorobenzene	O-NP39
	Oxolate	O-NP40
	Hypophosphoric acid	O-NP41
	O-Xylene dichloride	O-NP42
	Tristearin	O-NP43
	β-Chloroacetic acid	O-NP44
	Chloroacetic acid	O-NP45
	Nitro naphthalene	O-NP46
	Trimyristin	O-NP47
	Palmatic acid	O-NP48
	Heptadecanoic acid	O-NP49
	α-Chloroacetic acid	O-NP50
	Bee wax	O-NP51
	Glycolic acid	O-NP52
	p-Bromophenol	O-NP53
	Azobenzene	O-NP54
	Acrylic acid	O-NP55
	Stearic acid	O-NP56
	Dinitrotoluene (2,4)	O-NP57
	Phenylacetic acid	O-NP58
	Thiosinamine	O-NP59
	Bromocamphor	O-NP60
	Benzylamine	O-NP61
	Durene	O-NP62
	Acetamide	O-NP63
	Methyl bromobrenzoate	O-NP64
	XilitoL	O-NP65
	α-Naphthol	O-NP66

	D-sorbitol	O-NP67
	Glautaric acid	O-NP68
	p-Xylene dichloride	O-NP69
	Methyl fumarate	O-NP70
	Catechol	O-NP71
	Quinone	O-NP72
	Acetanilide	O-NP73
	Succinic anhydride	O-NP74
	Erythritol	O-NP75
	Benzoic acid	O-NP76
	Stilbene	O-NP77
	Benzamide	O-NP78
	Sebacic acid	O-NP79
	Phthalic anhydride	O-NP80
	Phenacetin	O-NP81
	Alpha glucose	O-NP82

	Dimethyl terephthalate	O-NP83
	Trans -1.4-polybutadiene	O-NP84
	Maltitol	O-NP85
	Lactitol	O-NP86
	Acetyl – p-toluidene	O-NP87
	Adipic acid	O-NP88
	Phenyldrazone benzaldehyde	O-NP89
	Salicylic acid	O-NP90
	Benzanilide	O-NP91
	D-mannitol	O-NP92
	Hydroquinone	O-NP93
	Potassium thiocynate	O-NP94
	GalactitoL	O-NP95
	Myo-Inositol	O-NP96

Inorganics	**Composition**	**Code**
HYDRATED SALTS	LiClO3·3H2O	I-SH1
	K2HO4.6H2O	I-SH2
	KF·4H2O	I-SH3
	Mn(NO3)2·6H2O	I-SH4
	LiBO2.8H2O	I-SH5
	FeBr3·6H2O	I-SH6
	CaCl2·12H2O	I-SH7
	LiNO3·2H2O	I-SH8
	LiNO3·3H2O	I-SH9
	Na2CO3·10H2O	I-SH10
	Na2SO4·10H2O	I-SH11
-	KFe(SO4)2·12H2O	I-SH12
	CaBr2·6H2O	I-SH13
	LiBr2·2H2O	I-SH14
	Zn(NO3)2·6H2O	I-SH15
	FeCl3·6H2O	I-SH16
	Mn(NO3)2·4H2O	I-SH17
	Na2HPO4·12H2O	I-SH18
	CoSO4·7H2O	I-SH19
	KF·2H2O	I-SH20
	MgI2·8H2O	I-SH21
	CaI2·6H2O	I-SH22
	K2HPO4·7H2O	I-SH23
	Zn(NO3)2·4H2O	I-SH24
	Mg(NO3)·4H2O	I-SH25
	Ca(NO3)·4H2O	I-SH26
	Fe(NO3)3·9H2O	I-SH27
	Na2SiO3·4H2O	I-SH28
	K2HPO4·3H2O	I-SH29
	Na2S2O3·5H2O	I-SH30
	MgSO4·7H2O	I-SH31
	Ca(NO3)2·3H2O	I-SH32
	Zn(NO3)2·2H2O	I-SH33
	FeCl3·2H2O	I-SH34
	Ni(NO3)2·6H2O	I-SH35
	MnCl2·4H2O	I-SH36
	MgCl2·4H2O	I-SH37
	CH3COONa·3H2O	I-SH38
	Fe(NO3)2·6H2O	I-SH39
	NaAl(SO4)2·10H2O	I-SH40
	NaOH·H2O	I-SH41
	Na3PO4·12H2O	I-SH42
	LiCH3COO·2H2O	I-SH43
	Al(NO3)2·9H2O	I-SH44
	Ba(OH)2·8H2O	I-SH45
	Al2(SO4)3·18H2O	I-SH46
	Al(NO3)3·8H2O	I-SH47
	Mg(NO3)2·6H2O	I-SH48
	KAl (SO4)2·12H2O	I-SH49
	(NH4)Al(SO4)·6H2O	I-SH50
	Na2S·5/2 H2O	I-SH51
	CaBr2·H2O	I-SH52
	Al2(SO4)3·6H2O	I-SH53
	MgCl2·6H2O	I-SH54
	Mg(NO3)·H2O	I-SH55
	NaC2H3O2·3H2O	I-SH56
	LiNO3	I-SH57
	NaNO2	I-SH58
	NaNO3	I-SH59
	RbNO3	I-SH60
	NaOH	I-SH61
	KNO3	I-SH62
	KOH	I-SH63
	$CsNO_3$	I-SH64
	AgBr	I-SH65
	LiOH	I-SH66
	$PbCl_2$	I-SH67
	LiBr	I-SH68
	$Ca(NO_3)_2$	I-SH69
	Ba(NO3)2	I-SH70
	Sr(NO3)2	I-SH71
	LiCl	I-SH72
	CsBr	I-SH73
	CsCl2	I-SH74
	FeCl2	I-SH75
	RbBr	I-SH76
	CsF	I-SH77
	MgBr2	I-SH78
	MgCl2	I-SH79
	RbCl	I-SH80
	Li2CO3	I-SH81
	KBr	I-SH82
	CaBr2	I-SH83
	NaBr	I-SH84
	KCl	I-SH85
	CaCl2	I-SH86
	RbF	I-SH87

	NaCl	I-SH88
	PbF2	I-SH89
	LiF	I-SH90
	Na2CO3	I-SH91
	Li2SO4	I-SH92
	KF	I-SH93
	Na2SO4	I-SH94
	K2CO3	I-SH95
	BaCl2	I-SH96
	K2CrO4	I-SH97
	NaF	I-SH98
	PbSO4	I-SH99
INORGANIC AND METALS	H2O	I-IN1
	POCl3	I-IN2
	D2O	I-IN3
	SbCl5	I-IN4
	H2SO4	I-IN5
	IC(β)	I-IN6
	MOF6	I-IN7
	SO3(α)	I-IN8
	IC(α)	I-IN9
	P4O6	I-IN10
	H3PO4	I-IN11
	Cs	I-IN12
	Ga	I-IN13
	AsBr35	I-IN14
	SnBr4	I-IN15
	BI3	I-IN16
	SO3(β)	I-IN17
	TiBr4	I-IN18
	H4P2O6	I-IN19
	SO3 (γ)	I-IN20
	NaOH	I-IN21
	SbCl3	I-IN22
	Na	I-IN23
	Li	I-IN24
	Sn91Zn9	I-IN25
	Tin	I-IN26
	Bismuth	I-IN27
	Pb	I-IN28
	Zn	I-IN29
	Zn2Mg	I-IN30
	Mg	I-IN31
	Al	I-IN32
	Mg2Cu	I-IN33
	Cu	I-IN34

Eutectics	PCM	Composition	Code
METAL ALLOYS.	Ga-In-Zn		E-ME1
	Ga-In		E-ME2
	Ga-Sn-Zn		E-ME3
	Ga 74-Sn-Cd		E-ME4
	Ga-Sn		E-ME5
	Ga 93-Sn-Cd		E-ME6
	Ga-Zn		E-ME7
	Ga -GaSb		E-ME8
	Cerrolow		E-ME9
	Bi–Cd–In		E-ME10
	Cerrobend		E-ME12
	Bi–Pb–In		E-ME13
	Bi–In		E-ME14
	Bi–Pb–tin		E-ME15
	Bi–Pb		E-ME16
INORG EUTECTIC	CaCl2·6H2O + CaBr2·6H2O		E-II1
	CaCl2 + MgCl2·6H2O		E-II2
	Ca(NO3)·4H2O + Mg(NO3)3·6H2O		E-II3
	AlCl3 + BaCl2 + NaCl		E-II4
	Mg(NO3)3·6H2O + NH4NO3		E-II5
	Mg(NO3)3·6H2O + MgCl2·6H2O	59/41	E-II6
	Mg(NO3)3·6H2O + MgCl2·6H2O	50/50	E-II7
	Mg(NO3)3·6H2O + Al(NO3)2·9H2O		E-II8
	Mg(NO3)2·6H2O + MgBr2·6H2O		E-II9
	AlCl3 + LiCl		E-II10
	LiNO3 + NH4NO3 + NaNO3		E-II11
	LiNO3 + NH4NO3 + KNO3		E-II12
	LiNO3 + NH4NO3 + NH4Cl		E-II13
	AlCl3 + KCl + LiCl		E-II14
	AlCl3 + KCl + NaCl		E-II15
	AlCl3 + NaCl + TlCl3		E-II16
	AlCl3 + KCl + TlCl3		E-II17
	AlCl3 + KCl + TlCl3		E-II18
	LiNO3 + NaNO3 + KNO3 + Sr(NO3)2		E-II19
	LiNO3 + KNO3	33/67	E-II20
	LiNO3 + KNO3	32/68	E-II21
	KNO3 + NaNO2 + NaNO3		E-II22
	LiNO3 + NaNO3 + KCla		E-II23
	LiNO3 + KCla		E-II24
	NaOH + KOH		E-II25
	LiNO3 + LiCl + NaNO3		E-II26
	LiNO3 + NaNO3		E-II27
	LiNO3 + NaNO3		E-II28
	LiNO3 + NaNO3 + Sr(NO3)2		E-II29

	KNO3 + NaNO2		E-II30
	LiNO3–KNO3	33/67	E-II31
	LiNO3–KNO3	31.7/68.3	E-II32
	KNO3–NaNO2–NaNO3	53/40/7	E-II33
	LiNO3–NaNO3–KCla	55.4/4.5/40.1	E-II34
	LiNO3–KCla	58.1/41.9	E-II35
	NaOH–KOH	50/50	E-II36
	LiNO3–LiCl–NaNO3	47.9/1.4/50.7	E-II37
	LiNO3–NaNO3	57/43	E-II38
	LiNO3–NaNO3	49/51	E-II39
	LiNO3–NaNO3–Sr(NO3)2	45/47/8	E-II40
	LiNO3–NaCla	87/13	E-II41
	LiOH–NaOH	30/70	E-II42
	KNO3–NaNO3	54/46	E-II43
	NaOH–NaNO2	20/80	E-II44
	NaOH–NaNO2	73/27	E-II45
	NaOH–NaCl–NaNO3	78.1/3.6/18.3	E-II46
	NaOH–NaNO3	28/72	E-II47
	NaOH–NaCl–NaNO3	55.6/4.2/40.2	E-II48
	LiNO3–NaCla	93.6/6.4	E-II49
	LiCl–CsCl–KCl–RbCl	28.5/43.5/13.7/13.3	E-II50
	NaOH–NaNO3	81.5/18.5	E-II51
	LiOH–LiCl	63/37	E-II52
	NaOH–$NaNO_3$	59/41	E-II53
	LiCl–$Ca(NO_3)_2$	59.15/40.85	E-II54
	LiOH–LiCl	65.5/34.5	E-II55
	LiOH–LiCl–KCl	62/36.5/1.5	E-II56
	Na_2CO_3–NaOH–NaCl	6.6/87.3/6.1	E-II57
	NaCl–NaOH–$NaCO_3$	7.8/85.8/6.4	E-II58
	$NaNO_3$–NaCl–Na_2SO_4	86.3/8.4/5.3	E-II59
	NaF–$NaNO_3$–NaCl	5/87/8	E-II60
	KOH-LiOH	60/40 a	E-II61
	NaOH-NaCl-Na2CO3	77.2/16.2/6.6	E-II62
	LiCl-KCl-BaCl2	54.2/39.4/6.4	E-II63
	KNO3-KCl	96/4 a	E-II64
	LiCl-KCl-LiCO3-LiF	47/47/3/2	E-II65
	KNO3-KBr-KCl	80/10/10 a	E-II66
	LiCl-NaCl-KCl	43/33/24 a	E-II67
	LiCl-KCl	58/42	E-II68
	MnCl2-KCl-NaCl	45/28.7/26.3,	E-II69
	Li2MoO4-LiVO3-LiCl-Li2SO4-LiF	27/25/23/18/6	E-II70
	LiCl-LiVO3-LiF-Li2SO4-Li2MO4	42/17/17/12/12	E-II71
	NaOH-NaCl	80/20	E-II72
	MgCl2-NaCl-KCl	55/25/20	E-II73
	MgCl2-NaCl-KCl	45.4/33/21.6	E-II74
	KCl-MnCl2-NaCl	45.5/34.5/20	E-II75

	MgCl2-NaCl-KCl	50/30/20	E-II76
	MgCl2-NaCl-KCl	51/27/22	E-II77
	Li2CO3-K2CO3-Na2CO3	32.1/34.5/33.4	E-II78
	KCl-MnCl2-NaCl	37.7/37.3/25	E-II79
	Zn-Mg	53,7/46,3	E-II80
	Zn-Mg	51/49	E-II81
	Zn-Al	96/4	E-II82
	Li2CO3-K2CO3-Na2CO3	32/35/33	E-II83
	Mg-Cu-Zn	55/28/17	E-II84
	Al-Mg-Zn	59/35/6	E-II85
	Mg-Cu-Zn	60/25/15	E-II86
	Mg-Cu-Ca	52/25/23	E-II87
	Al-Si-Sb	86/10/4	E-II88
	Mg-Al	35/65	E-II89
	Al-Cu-Mg	61/33/6	E-II90
	Al-Si-Cu-Mg	64/5/28/2	E-II91
	Al-Cu-Mg-Zn	54/22/18/6	E-II92
	Al-Cu-Si	68,5/26,5/5	E-II93
	Al-Cu-Sb	64/34/2	E-II94
	Al-Cu	67/33	E-II95
	Al-Si-Mg	83/12/5	E-II96
	Al-Si	88/12	E-II97
	Cu-Al-Si	49/46/5	E-II98
	Al-Cu-Si	65/30/5	E-II99
	Al-Si-Sb	86/10/4	E-II100
	Al-Si	88/12	E-II101
	Si-Al	80/20	E-II102
	Zn-Cu-Mg	49/45/6	E-II103
	Cu-P	91/9	E-II104
	Cu-Zn-P	69/17/14	E-II105
	Cu-Zn-Si	74/19/7	E-II106
	Cu-Si-Mg	56/27/17	E-II107
	Mg-Ca	84/19	E-II108
	Mg-Si-Zn	47/38/15	E-II109
	Cu-Si	80/20	E-II110
	Cu-P-Si	83/10/7	E-II111
	Si-Mg-Ca	49/30/21	E-II112
	Si-Mg	56/44	E-II113
INORG/ORG EUT.	Triethylolethane + water + urea		E-IO1
	Sodium Ethanoate + Urea		E-IO2
	Urea + Nitrato de Amonio		E-IO3
	Napthalene + benzoic acid		E-IO4
	Urea + Bromuro de Amonio		E-IO5
PARAFFIN EUT.	Tetradecane+docosane		E-PO1
	Tetradecane+geneicosane		E-PO2

	Pentadecane+heneicosane		E-PO3
	Tetradecane+octadecane		E-PO4
	Pentadecane+octadecane		E-PO5
	Octadecane+heneicosane		E-PO6
	Pentadecane+docosane		E-PO7
	Octadecane+docosane		E-PO8
	Tetradecane (91.67 mole.%)+hexadecane (8.33 mole.%)		E-PO9
ORGAN. EUT.	Butyl palmiate (49 wt%)+butyl stearate (48 wt%)+other (3 wt%)		E-OO1
	Carpic acid+Lauric acid		E-OO2
	Carpic acid (655 mol%)+lauric acid (35 mol.%)		E-OO3
	Carpic acid (61.5 wt%)+lauric acid (38.5 wt%)		E-OO4
	Carpic acid (73.5 wt%)+myristic acid (26.5 wt%)		E-OO5
	Carpic acid (75.2 wt%)+palmitic acid (24.8 wt%)		E-OO6
	Methyl palmiate (65–90 wt%)+methyl stearate (35–10 wt%)		E-OO7
	myristic acid + Neodecanoic acid		E-OO8
	Carpic acid (86.6 wt%)+stearic acid (13.4 wt%)		E-OO9
	Acetamide + Urea		E-OO10
	Triethylolethane + urea		E-OO11
	Lauric acid (62.6 wt%)+myristic acid (37.4 wt%)		E-OO12
	Lauric acid (80.0 wt%)+palmitic acid (20.0 wt%)		E-OO13
	Lauric acid (64.0 wt%)+palmitic acid (36.0 wt%)		E-OO14
	Lauric acid (77.0 wt%)+palmitic acid (23.0 wt%)		E-OO15
	Lauric acid+stearic acid		E-OO16
	Lauric acid (66.0 wt%)+myristic acid (34.0 wt%)		E-OO17
	Lauric acid (69.0 wt%)+palmitic acid (31.0 wt%)		E-OO18
	Lauric acid (75.5 wt%)+stearic acid (24.5 wt%)		E-OO19
	Lauric acid (75.5 wt%)+stearic acid (24.5 wt%)		E-OO20
	Myristic acid (51 wt%)+Palmitic acid (49 wt%)		E-OO21
	Myristic acid (58 wt%)+palmitic acid (42 wt%)		E-OO22
	Myristic acid (65.7 wt%)+stearic acid (34.7 wt%)		E-OO23
	Myristic acid (64.0 wt%)+stearic acid (36.0 wt%)		E-OO24
	MA3PA2 (myristic acid+palmitic acid)		E-OO25
	MA2SA (myristic acid+stearic acid)		E-OO26
	Palmitic acid (64.9 wt%)+stearic acid (35.1 wt%)		E-OO27
	PeASA (pentadecane acid+stearic acid)		E-OO28
	Palmitic acid+stearic acid		E-OO29
	Palmitic acid (64.2 wt%)+stearic acid (35.8 wt%)		E-OO30
	Stearic acid (65 wt%)+palmitic acid (27.5 wt%)+other fatty acids (5.5 wt%)—emery 419		E-OO31
	Palmitic acid (50 wt%)+stearic acid (45.5 wt%)+other fatty acids (4.5 wt%)—emersol 131		E-OO32
	PASA (palmitic acid+stearic acid)		E-OO33
	Stearic acid (83 wt%)+palmitic acid (11 wt%)+other fatty acids (6% wt%)—emersol 149		E-OO34
	Acetamide + Stearic Acid		E-OO35
	Stearic acid (95 wt%)+palmitic acid (5 wt%)—emersol 152		E-OO36

Sigue tus principios hasta alcanzar tus finales.

aprende de cuanto el camino te depare,

y abraza tus errores,

son la semilla de tu siguiente logro.

Patricia Royo