

# Northumbria Research Link

Citation: Lizcano-González, Víctor A., Kafarov, Viatcheslav V. and Mahkamov, Khamid (2022) Production of Fatty Esters from Palm Oil By-Products for use as Phase Change Materials. Chemical Engineering Transactions, 94. pp. 331-336. ISSN 1974-9791

Published by: AIDIC

URL: <https://doi.org/10.3303/CET2294055> <<https://doi.org/10.3303/CET2294055>>

This version was downloaded from Northumbria Research Link: <https://nrl.northumbria.ac.uk/id/eprint/50781/>

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: <http://nrl.northumbria.ac.uk/policies.html>

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)

# Production of Fatty Esters from Palm Oil By-Products for use as Phase Change Materials

Víctor A. Lizcano-González<sup>a</sup>, Viatcheslav V. Kafarov<sup>a,\*</sup>, Khamid Mahkamov<sup>b</sup>

<sup>a</sup>Department of Chemical Engineering, Carrera 27 Calle 9, Universidad Industrial de Santander, Bucaramanga, Colombia

<sup>b</sup>Department of Mechanical and Construction Engineering, Sutherland Building Newcastle-upon-Tyne NE1 8ST, Northumbria University, United Kingdom  
 kafarov@uis.edu.co

Palm stearin is the heavy fraction obtained during palm oil refining. It consists mainly of saturated fatty acids and is often an unwanted by-product that reduces the economic efficiency of the processes. Although it is currently used in the manufacture of margarine or industrial vegetable fats, the increase in palm oil production will lead to higher production of palm stearin. The composition, low cost and physicochemical characteristics of palm stearin make it an ideal raw material for obtaining phase change materials for thermal energy storage in solar thermal energy systems. This work explores the esterification of hydrogenated palm stearin (HPS) for obtaining phase change materials with suitable properties for application. The esterification conditions were studied using low and high molecular weight alcohols, like ethanol, butanol and cetyl alcohol, according to Fischer's esterification principles. The esters formation was characterized by attenuated total reflectance infrared spectroscopy. For both HPS and products obtained, melting and solidification temperatures and enthalpies, and heat capacity were determined by DSC according to ASTM E793-06(2018) and ASTM E1269-11(2018). A crude wax was obtained by esterification of the fatty acids present in palm stearin in all cases. Among the esters produced, the one obtained by using cetyl alcohol, which has a melting temperature of 55.9 °C and an enthalpy of fusion of 257.26 kJ/kg, stands out. This novel PCM is presumed to have an optimal performance for heat storage applications in low temperature solar thermal systems (50°C - 90°C), for hot water supply and space conditioning.

## 1. Introduction

A highly viable alternative for heat supply are solar thermal systems for domestic and small business applications, which accumulate solar energy during the day to release it at night (Fleischer, 2015). Several studies have been reported worldwide where different Solar Thermal Energy Storage Systems (STESS) have been evaluated (Sarbu and Sebarchievici, 2018). Most of STESS reported in the scientific literature focus on hot water supply and reduction or elimination of heating systems (Sharif et al., 2015). In several applications, the use of STESS is complemented by passive thermal energy management measures, which may include the use of heat storage materials (Liu, 2017). In order to extend the implementation of STESS, phase change materials (PCM) that meet the technical and economic requirements must be continuously developed (Riffat et al., 2015).

In STESS, PCM, which can be made from agricultural waste and inedible organic products, are used as heat storage materials (Abhat, 1983). Some desirable characteristics for these materials are: A high value of heat of fusion and specific heat per unit volume and weight, a melting point appropriate to the application, a low vapor pressure (< 1 bar) at operating temperature, chemical stability and non-corrosiveness, a PCM must not be hazardous, highly flammable, or poisonous, a PCM must have reproducible crystallization without degradation, a PCM must have a small degree of supercooling and a high rate of crystal growth, a PCM should have a small volume variation during solidification, a high thermal conductivity, a PCM must be abundant and low cost (Kenisarin and Mahkamov, 2007).

In recent years, the development of PCMs of animal or plant origin has been investigated, with fatty acids, fatty acid mixtures, fatty acid esters, polymers, process residues and by-products, polyols and other sugars emerging as having high potential (Peñalosa García et al., 2015). The use of organic materials of animal or plant origin, preferably autochthonous, allows, among other advantages, the reduction of costs and lowering the risk of environmental pollution (Ravotti et al., 2019). In addition, it can contribute to the valorisation of numerous agro-industrial production chains (Teles dos Santos et al., 2016). The use of beeswax as a phase change material has been reported, with an enthalpy of fusion of 145.62 kJ/kg and a melting temperature of 62.28 °C (Putra et al., 2019). Also, the characterization of encapsulated carnauba wax for its potential use as a phase change material was reported, with a melting temperature of 78 °C and a melting enthalpy of 200 kJ/kg (Paulo et al., 2019). The characterization of various fatty acids for their potential use as phase change material has also been reported, using samples with high purity and costs above 3.35 USD/kg (Anand et al., 2021). It highlights the potential of vegetable oils to produce phase change materials, especially from the fatty acids contained in them, considering the growth of palm oil and sunflower oil industries (Yuan et al., 2014).

Despite the various advantages of organic PCMs of plant or animal origin, they have technical disadvantages for their application, being the most relevant its low thermal conductivity (Kenisarin et al., 2019). Another important disadvantage is the variability in compositions (Gunstone, 2013). Because of these disadvantages, the continuous search for organic, abundant, and low-cost sources of PCM has been of interest in recent years. The present work aims to evaluate the potential of hydrogenated palm stearin (HPS) as a raw material for fatty esters production. Palm stearin (PS) is obtained during the refining process of crude palm oil, specifically during the removal of solid material (Winterization) (Andreia Schäfer De Martini Soares et al., 2009). In many cases the PS content represents up to 30 % by weight of the oil, presenting a fatty acid profile rich in palmitic acid (68.3 %) and oleic acid (20.6 %) (Zou et al., 2012). In order to increase the content of saturated fatty acids, especially stearic acid, complete hydrogenation of palm stearin can be carried out with a variation in the thermal properties of this material (Patterson, 2011). Due to the above, the present work aims to obtain phase change materials from HPS and three different alcohols. The characterisation by ATR-FTIR of the obtained esters is presented, as well as the profiles obtained by DSC. Additionally, the thermal properties of the synthesised material with the highest latent heat storage capacity are compared with the properties of beeswax as an alternative PCM of agro-industrial origin. Beeswax was selected as one of the agro-industrial products available on the market with suitable characteristics for use as a PCM. Although carnauba wax has been studied more extensively as a potential PCM, its cost is much higher than that of beeswax (Singh et al., 2020).

## 2. Methodology

The synthesis of the fatty esters and their thermal characterization was carried out as described below.

### 2.1 Synthesis of fatty esters

Equimolar amounts of fatty acids and alcohols were used for all reactions, avoiding excess of any of the reagents. The molecular weight of hydrogenated palm stearin was calculated according to its chemical composition (Andreia Schäfer De Martini Soares et al., 2009). A total of 5 g of reagents were used for all experiments. The reactions were carried out for 1 h at 96 °C with constant stirring. H<sub>2</sub>SO<sub>4</sub> was used as a catalyst for the reaction. Reflux condensers were used to avoid losses of reagents. After the reaction time had elapsed, the reaction products were washed with water, which was subsequently removed by decantation. The product obtained was oven dried for 2 h at 105 °C (Ravotti et al., 2018).

### 2.2 Characterization of samples by ATR-FTIR

A Shimadzu IRTracer-100 spectrophotometer equipped with an ATR cell was used. The analysis was performed for a wavelength from 400 cm<sup>-1</sup> to 4,000 cm<sup>-1</sup>. A resolution of 4 cm<sup>-1</sup> was used. For each spectrum, the sample was scanned 25 times with a signal-to-noise ratio of 60,000:1.

### 2.3 Temperatures and enthalpies of fusion and crystallization

The determination of melting and crystallization temperatures as well as the estimation of the enthalpy of fusion and solidification was carried out by differential scanning calorimetry (DSC). A Q10 calorimeter (TA Instruments) was used. The equipment allows an operating range from -180 °C to 725 °C with a calorimetric accuracy of 1% and a sensitivity of 1 µW. The procedure described in the ASTM E793-06 Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry was followed. Briefly, the samples were rapidly heated from room temperature up to 150 °C. Subsequently it was cooled down to -50 °C at a rate of change of 5 °C/min. The sample was heated again from -50 °C to 150 °C/min at a rate of change of 10 °C/min (ASTM International, 2018a). Experimental data were computed using TRIOS 5.1.1 software (TA Instruments).

## 2.4 Heat capacity

The heat capacity of the materials was calculated according to ASTM E1269 - 11 Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry. A Q10 calorimeter (TA Instruments) was used. A sapphire standard with a mass of 26.1 mg and a heating rate of 5 °C/min were used (ASTM International, 2018b).

## 3. Results

The results obtained for the thermal and functional group characterisation are presented as follows.

### 3.1 Synthesis of fatty esters

Figure 1 shows images of the fatty esters obtained and beeswax.

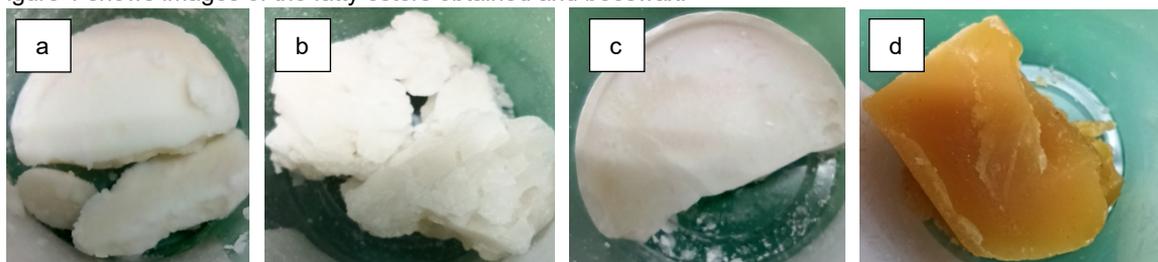


Figure 1: Photographs of fatty esters obtained from hydrogenated palm stearin and a) ethyl alcohol (HPS-EA), b) butyl alcohol (HPS-BA) and c) cetyl alcohol (HPS-CA), d) beeswax (BW).

According to its physical appearance, the ester obtained from palm stearin and cetyl alcohol has a greater hardness, being even more rigid than beeswax. The esters obtained from butyl and ethyl alcohol have a soft consistency. The white color observed for the samples is almost identical to the shade shown by palm stearin.

### 3.2 Characterization of samples by ATR-FTIR

Figure 2 shows the spectra obtained for the characterization of the samples by ATR-FTIR.

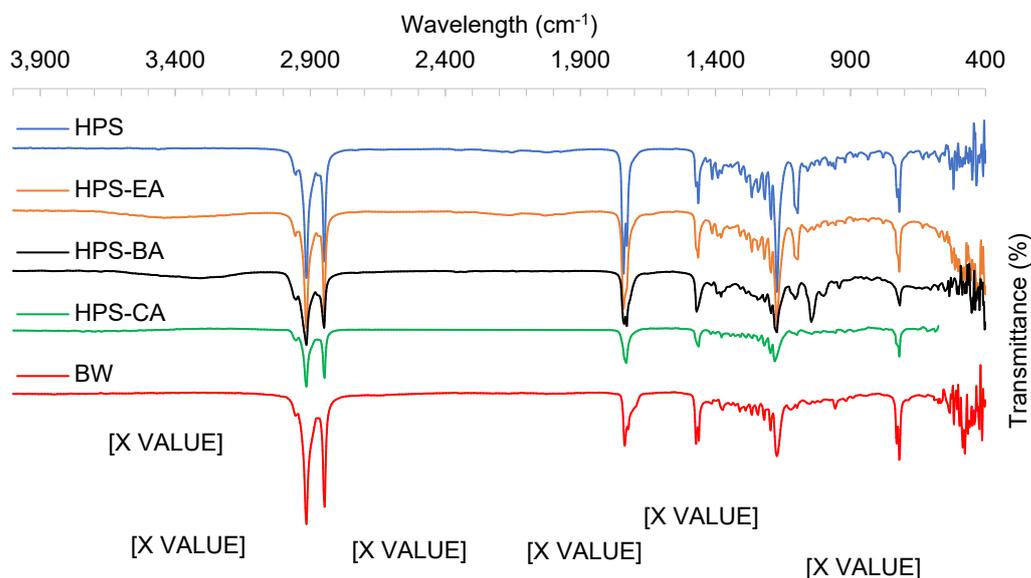


Figure 2: ATR-FTIR of prepared samples and beeswax. The main peaks of interest for correct identification of esters are the stretch of C=O at 1,736  $\text{cm}^{-1}$  for esters, the broad peaks between 3,600-3,100  $\text{cm}^{-1}$  and 3,000-2,300  $\text{cm}^{-1}$  from O-H stretch of alcohols and carboxylic acids and the peak at 1,177  $\text{cm}^{-1}$  from C-O-C stretch in esters.

The presence of the ester group is confirmed by the peaks at wavenumbers  $1,736\text{ cm}^{-1}$  and  $1,177\text{ cm}^{-1}$ . The higher intensity of this signal for hydrogenated palm stearin is due to the presence of triglycerides, which are esters of fatty acids and glycerol. The broad peaks between  $3,600\text{--}3,100\text{ cm}^{-1}$  and  $3,000\text{--}2,300\text{ cm}^{-1}$  from O-H stretch of alcohols and carboxylic acids and the peak at  $1,177\text{ cm}^{-1}$  from C-O-C stretch in esters. It is remarkable the similarity of the spectrum obtained for beeswax and for the HPS-CA ester, indicating that as the transesterification reaction proceeds a decrease of the signals at  $1,736\text{ cm}^{-1}$  and  $1,177\text{ cm}^{-1}$  can be expected.

### 3.3 Temperatures and enthalpies of fusion and crystallization

Figure 3 shows the profiles obtained by differential scanning calorimetry for all samples.

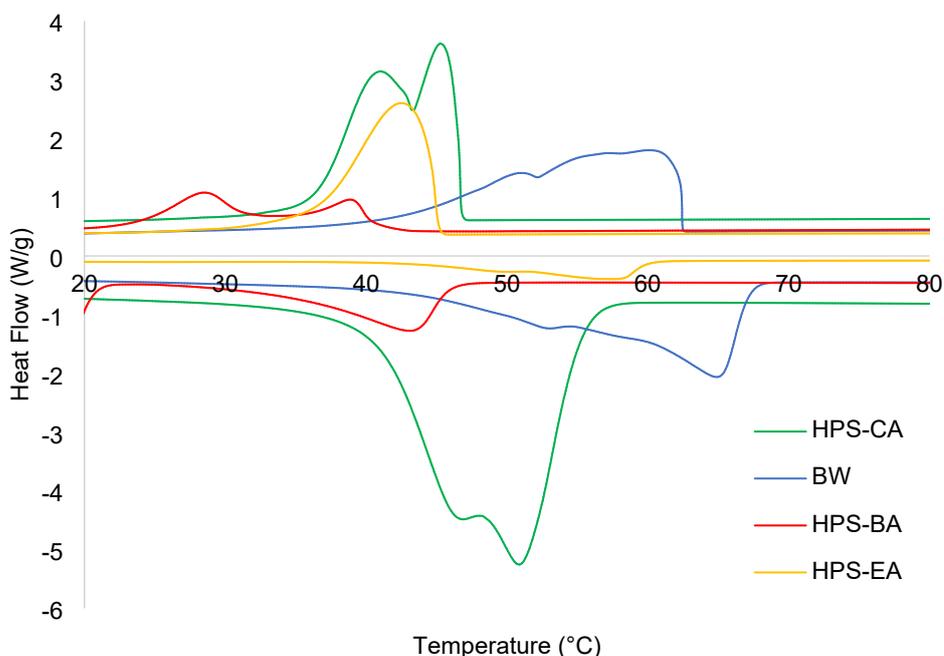


Figure 3: Profiles obtained by differential scanning calorimetry for HPS-EA, HPS-BA, HPS-CA and BW. The HPS-CA ester has the highest enthalpy of fusion value, reaching  $257.26\text{ kJ/kg}$  with a melting temperature of  $55.9\text{ }^{\circ}\text{C}$ . Beeswax has an enthalpy of fusion of  $233.8\text{ kJ/kg}$  and a melting temperature of  $64.9\text{ }^{\circ}\text{C}$ .

When comparing the curves, differences between the samples can be observed, however, the absence of single, defined peaks indicates the presence of different substances in all samples. For beeswax, two broad, low peaks are present, indicating a melting and solidification process over a wide temperature range. For the HPS-EA sample, two well-defined peaks are present, although the signal obtained during crystallization has a larger area than the signal during the melting process. For the HPS-BA sample, two distinct peaks are observed for the crystallization process and only one for the melting process. Finally, the highest signal is found for the HPS-CA sample, which was expected due to the higher molecular weight and melting point of the alcohol used. Although the HPS-CA sample appears to have two signal peaks, this can be treated as one. A comparison of the thermal parameters of the HPS-CA sample and beeswax is presented in Table 1. The HPS-CA sample had the highest enthalpy of fusion of the fatty esters prepared, making it more suitable for thermal energy storage.

Table 1: Thermal properties of fatty ester HPS-CA and beeswax. The HPS-CA sample has a 10% higher enthalpy of fusion value and a  $9\text{ }^{\circ}\text{C}$  lower melting temperature compared to the BW sample.

Property	HPS-CA	BW
Melting temperature ( $^{\circ}\text{C}$ )	55.9	64.9
Crystallization temperature ( $^{\circ}\text{C}$ )	45.6	60.3
Enthalpy of Fusion ( $\text{kJ/kg}$ )	257.26	233.8
Enthalpy of Crystallization ( $\text{kJ/kg}$ )	248.13	238.7

The melting temperature of HPS-CA is 9 °C lower than that of beeswax, yet its enthalpy of crystallization is 23.5 kJ/kg higher. Also, a hysteresis phenomenon is highlighted for both materials as the crystallization temperatures are lower than the melting temperatures. In the case of beeswax this difference is 5 °C while for HPS-CA the difference is 10 °C. Likewise, it is worth noting the higher latent heat energy storage capacity of the HPS-CA ester compared to refined wax A53, which has a melting enthalpy of 237.5 kJ/kg for a melting temperature of 53 °C (Dogkas et al., 2019). The enthalpy of fusion value obtained for the HPS-CA sample is significantly higher than the 177.1 kJ/kg reported for cetyl palmitate (Wang et al., 2020). The above, added to the fact that in the present work HPS is used with an approximate cost of 2.5 USD/kg and obtained from an agro-industrial by-product, shows the different advantages of this new PCM.

### 3.4 Specific Heat Capacity

Table 2 presents solid and liquid heat capacity values for HPS-CA fatty ester and beeswax.

Table 2: Solid and liquid heat capacity values for HPS-CA fatty ester and beeswax.

Temperature (°C)	Specific Heat Flow (W/g)				Specific Heat Capacity (kJ / kg K)		
	HPS-CA	BW	Empty Capsule	Sapphire	Sapphire	HPS-CA	BW
26.85	-0.232	-0.2214	-0.03296	-0.09079	0.7792	2.682	2.539
36.85	-0.2778	-0.2408	-0.03995	-0.09974	0.7999	3.182	2.687
76.85	-0.3072	-0.3265	-0.04081	-0.1132	0.8721	3.209	3.442
86.85	-0.3123	-0.3303	-0.03958	-0.1157	0.8878	3.181	3.391

Two temperature values below and above the melting points of the samples were selected in order to estimate the heat capacity of both solid and liquid. For beeswax, higher heat capacity values are observed for liquid than for solid. This trend is not present for the HPS-CA sample.

## 4. Conclusions

Materials with high fatty ester content were synthesised from hydrogenated palm stearin and different fatty alcohols. It is noted that due to the high ester content in hydrogenated palm stearin, caused by the presence of triglycerides, the reaction can be followed up by observing the signal at 1,117 cm<sup>-1</sup> in the ATR-FTIR analysis. From the samples obtained, the HPS-CA ester stands out with a melting temperature of 55.9 °C and a melting enthalpy of 257.26 kJ/kg, which is higher than the value reached by beeswax and those reported for some paraffine wax. Additionally, higher solid heat capacity values were presented for the HPS-CA sample than for beeswax (2.682 kJ/kg K, 3.182 kJ/kg K and 2.539 kJ/kg K, 2.687 kJ/kg K). The above, coupled with the higher enthalpy of fusion values achieved, show that the amount of heat to be stored in the same solar thermal energy storage system is higher if HPS-CA is used instead of beeswax. These first results show that it is possible to obtain phase change materials from agro-industrial by-products of the palm oil industry. It is therefore recommended to continue with the study of the esterification and transesterification process of saturated fatty acids, using high molecular weight fatty alcohols to develop a variety of PCM of agro-industrial origin. Likewise, it is recommended the development of purification methods for the esters obtained, to guarantee high purity and uniform thermal behaviour.

### Acknowledgments

The authors would like to thank The Royal Society for funding this research through the Enabling Harvesting of Solar Energy for Remote Applications in the Andes Region (LA-SOLAR ENHANCE) project. Special thanks to the School of Chemical Engineering of the Universidad Industrial de Santander for providing access to the materials and equipment necessary for the characterization of the samples.

### References

- Abhat A., 1983, Low temperature latent heat thermal energy storage: Heat storage materials, *Solar Energy* 30, 313–332.
- Anand A., Kant K., Shukla A., Chen C.-R., Sharma A., 2021, Thermal Stability and Reliability Test of Some Saturated Fatty Acids for Low and Medium Temperature Thermal Energy Storage, *Energies (Basel)* 14, 4509.

- Andreia Schäfer De Martini Soares F., Claro da Silva R., Caroline Guimarães da Silva K., Bertolessi Lourenço M., Ferreira Soares D., Antonio Gioielli L., 2009, Effects of chemical interesterification on physicochemical properties of blends of palm stearin and palm olein, *Food Research International* 42, 1287–1294.
- American Society for Testing Materials, 2018a, E793-06(2018) Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry, ASTM International, West Conshohocken, USA.
- American Society for Testing Materials, 2018b, E1269-11(2018) Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry, ASTM International, West Conshohocken, USA.
- Dogkas G., Konstantaras J., Koukou M.K., Stathopoulos V.N., Coelho L., Rebola A., 2019, Evaluating a prototype compact thermal energy storage tank using paraffin-based phase change material for domestic hot water production, *E3S Web of Conferences* 116, 00016.
- Fleischer A.S., 2015, *Thermal energy storage using phase change materials: Fundamentals and applications*, Springer Cham, Heidelberg, Germany.
- Gunstone F.D., 2013, Composition and Properties of Edible Oils, Chapter In: W Hamm, R J Hamilton, G Calliauw (Ed), *Edible Oil Processing (2nd Edition)*, Wiley-Blackwell, Chichester, UK, 1 – 40.
- Kenisarin M., Mahkamov K., 2007, Solar energy storage using phase change materials, *Renewable and Sustainable Energy Reviews* 11, 1913–1965.
- Kenisarin M., Mahkamov K., Kahwash F., Makhkamova I., 2019, Enhancing thermal conductivity of paraffin wax 53–57 °C using expanded graphite, *Solar Energy Materials and Solar Cells* 200, 110026.
- Liu X., 2017, Preparation and application of multicomponent composite phase change materials in building energy conservation, *Chemical Engineering Transactions* 62, 529–534.
- Patterson H.B.W., 2011, The Hydrogenation Reaction, in: *Hydrogenation of Fats and Oils*, Elsevier, Urbana, USA, 1–32.
- Paulo B.B., Andreola K., Taranto O., Ferreira A.D., Prata A.S., 2019, Coating approach for a Phase Change Material (PCM), *Powder Technology* 341, 147–156.
- Peñalosa García M.C., Zalba Nonay M.B., Lázaro Fernández A., 2015, Avances en determinación de propiedades termofísicas de materiales de cambio de fase, Búsqueda y análisis de nuevos materiales PCM-TES de bajo coste, Tesis Doctoral, Universidad de Zaragoza, Zaragoza, Spain.
- Putra N., Rawi S., Amin M., Kusriani E., Kosasih E.A., Indra Mahlia T.M., 2019, Preparation of beeswax/multi-walled carbon nanotubes as novel shape-stable nanocomposite phase-change material for thermal energy storage, *Journal of Energy Storage* 21, 32–39.
- Ravotti R., Fellmann O., Lardon N., Fischer L., Stamatou A., Worlitschek J., 2019, Analysis of Bio-Based Fatty Esters PCM's Thermal Properties and Investigation of Trends in Relation to Chemical Structures, *Applied Sciences* 9, 225.
- Ravotti R., Fellmann O., Lardon N., Fischer L.J., Stamatou A., Worlitschek J., 2018, Synthesis and investigation of thermal properties of highly pure carboxylic fatty esters to be used as PCM, *Applied Sciences (Switzerland)* 8, 1–18.
- Riffat S., Mempo B., Fang W., 2015, Phase change material developments: a review, *International Journal of Ambient Energy* 36, 102–115.
- Sarbu I., Sebarchievici C., 2018, A Comprehensive Review of Thermal Energy Storage, *Sustainability* 10, 191, DOI: 10.3390/su10010191.
- Sharif M.K.A., Al-Abidi A.A., Mat S., Sopian K., Ruslan M.H., Sulaiman M.Y., Rosli M.A.M., 2015, Review of the application of phase change material for heating and domestic hot water systems, *Renewable and Sustainable Energy Reviews* 42, 557–568.
- Singh R.P., Kaushik S.C., Rakshit D., 2020, Performance evaluation of charging process in a cascade latent heat storage system (C-LHSS) based on heat flux DSC results, *International Journal of Thermal Sciences* 151, 62-74.
- Teles dos Santos M., Viana I.S., Ract J.N.R., le Roux G.A.C., 2016, Thermal properties of palm stearin, canola oil and fully hydrogenated soybean oil blends: Coupling experiments and modelling, *Journal of Food Engineering* 185, 17–25.
- Wang C., Wang T., Hu Z., Cai, Z., 2020, Facile synthesis and thermal performance of cety palmitate/nickel foam composite phase change materials for thermal energy storage, *Journal of Energy Storage*, 28.
- Yuan Y., Zhang N., Tao W., Cao X., He Y., 2014, Fatty acids as phase change materials: A review, *Renewable and Sustainable Energy Reviews* 29, 482–49.
- Zou Y., Jiang Y., Yang T., Hu P., Xu X., 2012, Minor Constituents of Palm Oil: Characterization, Processing, and Application, in: *Palm Oil*, Elsevier, pp. 471–526.