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

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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 ASTME793-06(2018) and ASTME1269-11(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 overcooling 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_2SO_4 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^{-1} to 4,000 cm^{-1}. A resolution of 4 cm^{-1} 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

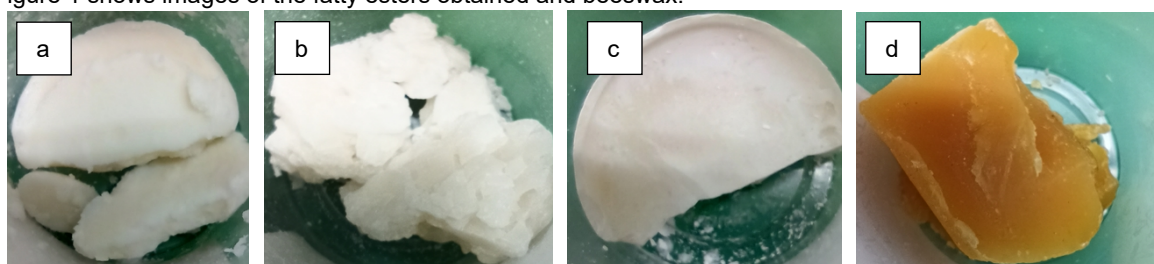Figure 1 shows images of the fatty esters obtained and beeswax.

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

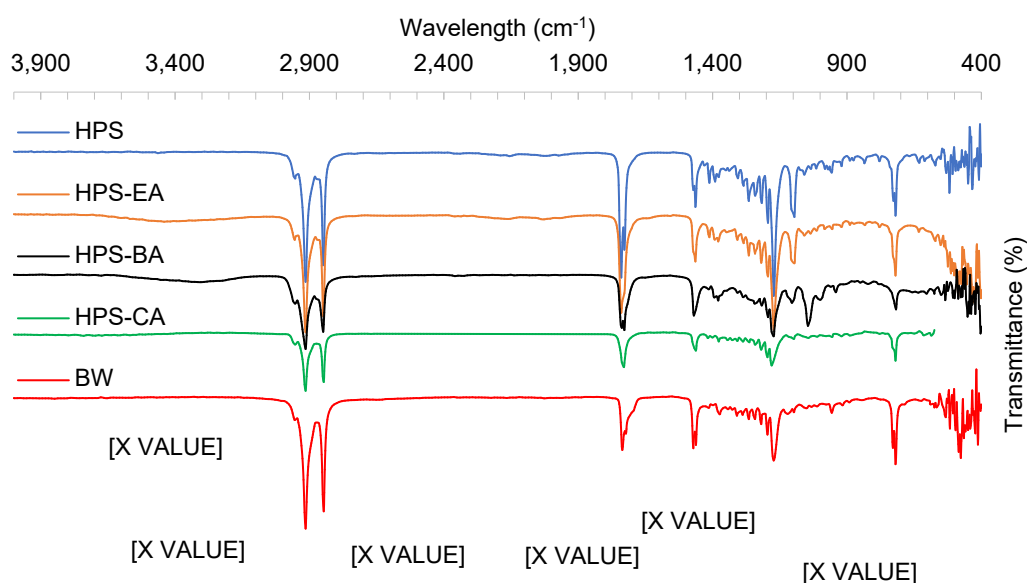Figure 2 shows the spectra obtained for the characterization of the samples by ATR-FTIR.

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 cm^{-1} for esters, the broad peaks between 3,600-3,100 cm^{-1} and 3,000-2,300 cm^{-1} from O-H stretch of alcohols and carboxylic acids and the peak at 1,177 cm^{-1} from C-O-C stretch in esters.

The presence of the ester group is confirmed by the peaks at wavelengths 1,736 cm^{-1} and 1,177 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 3,600-3,100 cm^{-1} and 3,000-2,300 cm^{-1} from O-H stretch of alcohols and carboxylic acids and the peak at 1,177 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 cm^{-1} and 1,177 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.
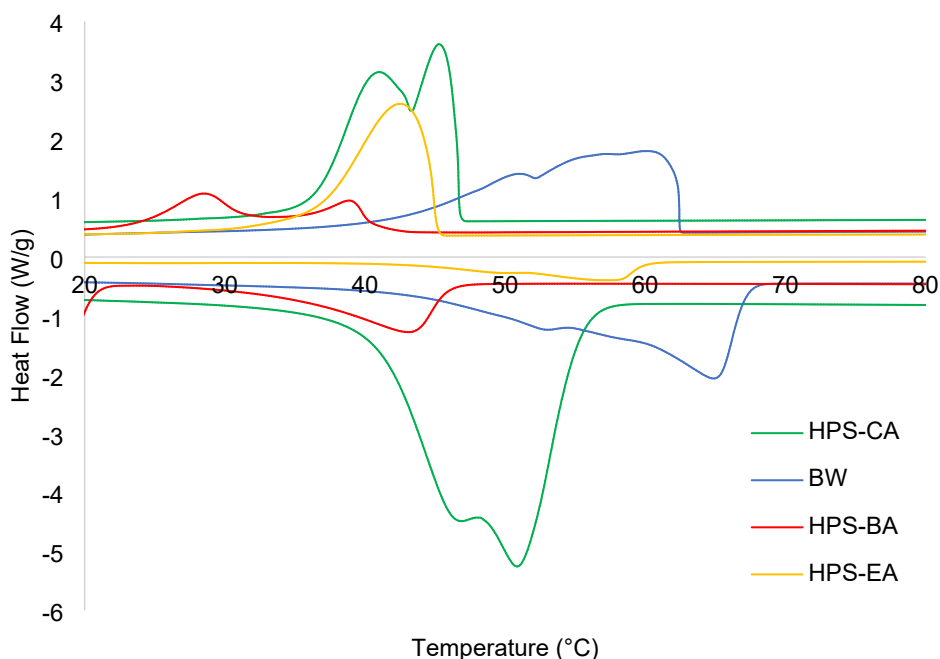

Figure 3: Profiles obtained by differential scanning calorimetry for HPS-EA, HPS-BA, HPS-CA and BW. The HPS-CA ester has the highest enthalpy of fusion value, reaching 257.26 kJ/kg with a melting temperature of 55.9 °C. Beeswax has an enthalpy of fusion of 233.8 kJ/kg and a melting temperature of 64.9 °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 °C lower melting temperature compared to the BW sample.

Property	HPS-CA	BW
Melting temperature (°C)	55.9	64.9
Crystallization temperature (°C)	45.6	60.3
Enthalpy of Fusion (kJ/kg)	257.26	233.8
Enthalpy of Crystallization (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^{-1} 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

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