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# Evaluation of Energy Storage Capacity of Vegetable Oils for Applications as Bio-PCMs

**Matheus Guedes**
**Raquel Soares**
**Maedson Silva**
**Lucas Lira**
**Taygoara Oliveira**
**Simone Monteiro***
**Antonio Brasil Junior**
Mechanical Engineering Department, University of Brasília, Brasília, DF 70910-900, Brazil
*Corresponding author: simonems@unb.br

***Abstract.*** *This work investigates the feasibility of using vegetable oils as PCMs for thermal comfort in building applications. Coconut oil was chosen as it solidifies at ambient conditions and its thermal properties, especially energy storage capacity was determined by T-history methodology. The accuracy and reproducibility of the experimental apparatus were validated using n-eicosane as standard. Samples were submitted to different cooling rates (mimicking variations of environmental conditions) to analyze the capacity of its energy storage. According to the results, the material's storage capacity was greater at slower cooling rates, because of different crystallization kinetics during the liquid-solid transition. Moreover, to check possible loss of performance, coconut oil was also exposed to more than 8 cycles of cooling/heating processes, corresponding 24-hour period. Furthermore, there is no variation in thermal properties even when the material is exposed to the studied successive heating and cooling processes. The results obtained corroborate coconut.*

***Keywords:*** *BioPCM, Vegetable oils, T-history*

## 1. INTRODUCTION

The continuous increase of population, estimated to reach 8.5 million in 2030 and 9.7 billions in 2050, led the United Nations to proposed a guideline, called the 2030 Agenda for Sustainable Development, in which the member countries agreed to foment different research areas to not only protect the planet from degradation but also to maintain peace and prosperity for the present and future generations. In this context, 17 Sustainable Development Goals (SDGs) were proposed one of which is to "ensure access to affordable, reliable, sustainable and modern energy for all" (Nations, 2023). Heat represents the largest share of global final energy consumption in 2021, surpassing both electricity (20%) and transportation (30%), making it the primary energy end use worldwide. The heat consumption in building applications accounts for 46% of the total end use energy consumed, primarily used for room and water heating, with a smaller portion allocated to cooking. Meanwhile, industrial processes constitute 51% of the energy consumed for heat generation IEA (2023). Given its importance, to ensure the availability of heat in a sustainable way, to deal with fluctuations of supply in energy, and to balance the the supply and demand the implementation of energy storage system capable allowing the the decoupling of consumption and production is of interest (GOV, 2023; Fatahi *et al.*, 2022).

Thermal energy storage (TES) is a process enabling the storage of heat (or cold) for further use (Venkateswarlu and Ramakrishna, 2021). Heat can be stored within two forms: as sensible or latent heat. The former is obtained by changing a material temperature, e.g. heating water within a tank. Storing sensible heat is difficult in terms of operational terms, because a large amount of substance is needed. The latter, which is the amount of energy released/absorbed during phase transition, is preferred because of its advanced energy storage capacity such as energy stored per mass (being far superior than sensible heat) and small volumetric variations (IRENA, 2023; Paroutoglou *et al.*, 2022). The materials that store energy through latent heat are called phase change materials (PCM). They are classified in three main categories: organic, inorganic, and eutectics. The organic PCMs can be: i) paraffin-based PCMs which present interesting energy-related properties but also great flammability and ii) non-paraffin organic PCMs which are formed by fatty acids, sugar alcohols, esters and glycols. Inorganic PCMs are salt hydrates and molten salts meanwhile eutectics are represented by mixtures of different substances that are combined in such a way to produce lower melting temperatures then the substances used to prepare the eutectic mixture (Faraj *et al.*, 2021).

Vegetable oils have recently gained the spotlight as possible substitutes for traditional PCMs (Paroutoglou *et al.*, 2022). They are formed by a mixture of triacylglycerols meaning that it does not present an unique melting point but rather a melting region (Wesdorp *et al.*, 2004). Some studies have already employed different vegetable oils such as coconut oil ((Jeon *et al.*, 2019; Faraj *et al.*, 2019; Wonorahardjo *et al.*, 2018), palm oil (Irsyad *et al.*, 2023), and sunflower oil (Baptista *et al.*, 2021). In the context, Brazil presents a good potential to employ vegetable oils as PCMs due its daily processing capacity (194,353 tons of vegetable oil per day (according to the Brazilian association of vegetable oil industries (ABIOVE, 2023)) being the Mato Grosso the principal processing state (Fig. 1).

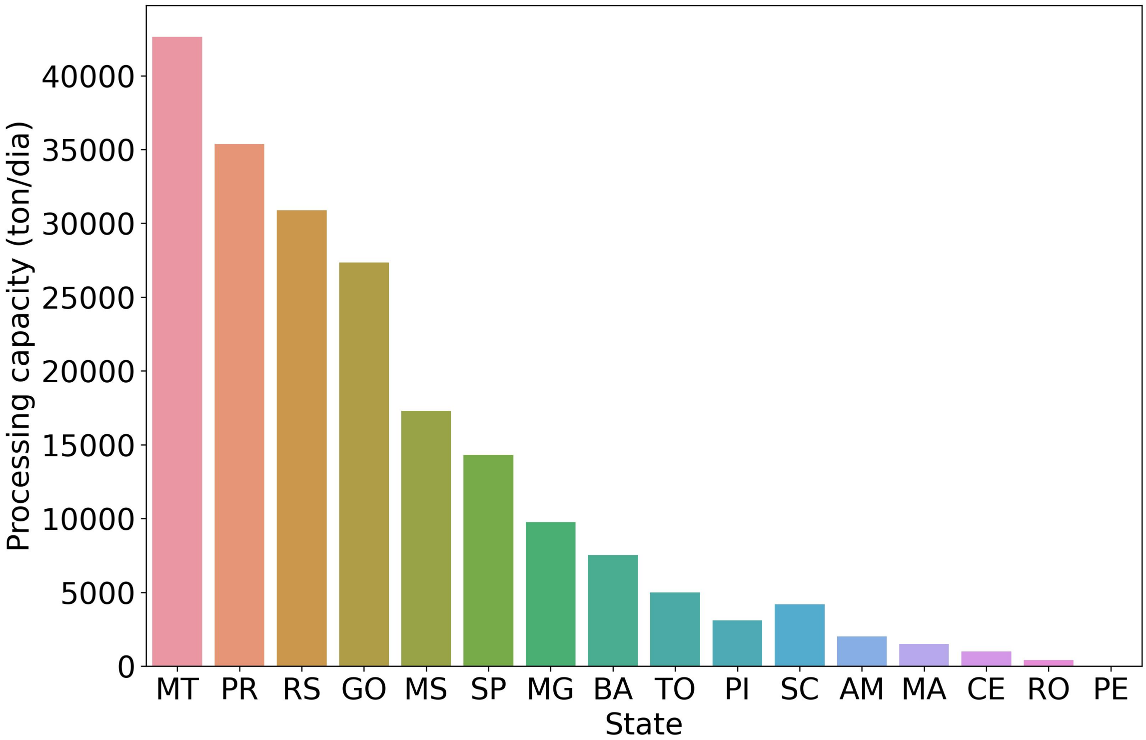


Figure 1. Brazilian vegetable oils processing capacity by state

However, one of the main barriers that refrained the application of vegetable oils as PCM is polymorphism (Ravotti *et al.*, 2020). Polymorphism is the capacity to present different crystalline configuration during the solidification process (Metin and Hartel, 2005). Since each crystalline conformation present its own characteristic transition region and enthalpy, controlling the solidification process is needed to adjust the thermophysical properties to the application. Nevertheless, it has been shown that such materials indeed offer great potential as PCMs, provided that not only that the material presents predictable behavior (an efficient control of polymorphism) but also that it does not loses its storage capacity nor its phase transition region within when submitted to multiple thermal cycles (Ravotti *et al.*, 2020).

The objective of this study was to assess the feasibility of utilizing vegetable oils as bioPCMs. Coconut oil was subjected to varying cooling rates, which simulated different ambient conditions that the material may encounter. This investigation aimed to highlight the significance of ambient temperature in determining the thermal energy storage capacity of these bioPCMs.

## 2. METHODOLOGY

### 2.1 T-history

The T-history methodology was proposed in 1999 (Yinping *et al.*, 1999) as an alternative to the Differential Scanning Calorimetry (DSC) analysis. By considering samples sizes greater than DSC not only bulk properties can be taken into account but also heat transfer effects such as conduction within the sample and convection with the ambient. The overall heat transfer phenomena relies on the Biot number and during the experimental stage, it was ensured that Biot number less than than 0.1 was obtained so that the hypotheses of independence of temperature distribution with spatial variation is valid. The energy balance during sensible heat region is given by

$$mc_p(T_i - T_f) = hA_c \int_{t_i}^{t_f} (T - T_\infty)dt, \tag{1}$$

where $m$ [kg] is the mass of the sample , $c_p$ [kJ kg$^{-1}$ K$^{-1}$] is the heat capacity of the phase considered (solid or liquid), $h$ [W m$^{-2}$ K$^{-1}$] is the convective heat-transfer coefficient, $A_c$ [m$^2$] is the convective heat-transfer area of a tube, $T_i$ [°C] and $t_i$[s] are, respectively, the temperature and the time where the sensible heat region starts, $T_f$ [°C] and $t_f$ [s] are, respectively, the temperature and the time where the sensible heat region ends

During the phase transition, the heat is represented by the phase transition enthalpy, $H_t$ [kJkg$^{-1}$]. The equation 1 is rewritten as

$$mH_t = hA_c \int_{t_1}^{t_2} T - T_\infty dt \tag{2}$$

where $t_1$ [s] and $t_2$ [s] represent, respectively, time of beginning and the end of latent heat region.

## 2.2 Experimental setup

The experimental setup (Fig. 2) consisted of two thermocouples type K, a temperature sensor (DS18B20), an Arduino UNO board, a thermostatic bath, two jacketed vessels connected in series, and two sample tubes, one filled with the investigated material and another one filled the reference material (water). One sample tube was filled with the material under investigation, while the other contained a reference material (water). Temperature measurements of the samples were taken using the thermocouples, while the sensor was used to measure the temperature of the thermostatic bath. Following calibration, the measurement equipment (thermocouples and sensor) was connected to an Arduino board to record the data.

Figure 2. Experimental setup used for T-history data acquisition

The jacketed vessels are connected in series and the system is connected to the bath through a recirculation system. The sample tube is placed in the vessel's inner compartment and the remainder is filled with water to ensure the heat transfer occurs. Coconut oil was submitted to the cooling profiles described on Tab. 1. N-eicosane was used as standard.

Table 1. Experimental conditions applied during data acquisition

| **Condition** | **Cooling rate** $[°\mathrm{Cmin}^{-1}]$ |
|---|---|
| 1 | 0.8 |
| 2 | 0.2 |

Each cooling profile respects a linear equation of the form

$$T_\infty(t) = \gamma t \tag{3}$$

where $\gamma$ represents the cooling rate in °C min$^{-1}$, $T_\infty$ [°C] represents the ambient temperature, and $t$ [s] is a time step.

## 3. RESULTS AND DISCUSSIONS

The T-history profile of n-eicosane (Fig.3) was used to validate the experimental setup proposed. The supercooling and melting temperatures were 36.9 °C and 37.4 °C, respectively. Thus, the subcooling degree (difference between supercooling and melting temperatures) was 0.5 °C, which is in accordance within the value of 0.68 found by DSC analysis (Wang *et al.*, 2021). Genovese *et al.* (2006) identified that during solidification, n-eicosane is capable of form a metastable phase that hinders capacity of the material to serve as a PCM. The authors reported that during DSC analysis, even with the formation of this intermediary phase, the solidification process started at 36.0 °C. The value reported in literature is close to the values found during the experiment proposed in this work (difference of 3.9%) which is considered acceptable since the T-history analysis is not as precise as DSC. Thus, the experimental apparatus can be used to determine the thermal properties of vegetable oils.

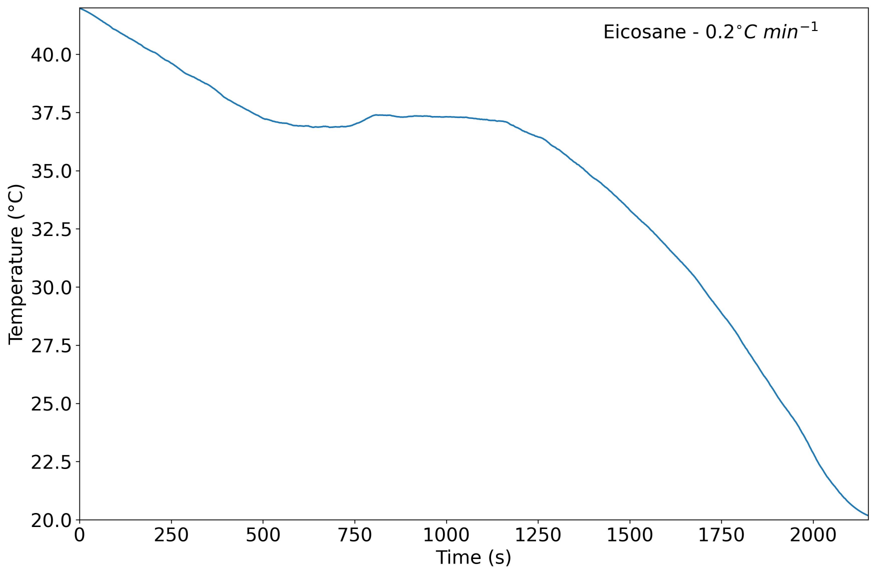


Figure 3. Validation of experimental apparatus: n-eicosane temperature vs time profile obtained with T-history methodology considering a cooling rate of 0.2 C $min^{-1}$

Figure 4 presents the temperature vs time behavior for the coconut oil. The T-history curve obtained for the cooling rate of 0.2 °C min$^{-1}$ exhibits a linear behavior until 35 °C, i.e. the temperature variation is proportional to the heat capacity of the material. From this point, there is a slightly reduction of temperature variation, more pronounced at the cooling rate at 0.2 °C min$^{-1}$ which is attributed to the beginning of solidification. Coconut oil's behavior can be attributed to its composition. The mixture of compounds it contains releases latent heat within that temperature range, resulting in a noticeable change in its temperature profile. Nakanishi and Ueno (2020) obtained different behaviors for a mixture of the main components from lard and palm oil (1,3-dioleoyl-2-palmitoyl-sn-glycerol (OPO) and 1,3-dipalmitoyl-2-oleoyl-sn-glycerol (POP), respectively). During solidification, there is a competition between arrangements for the molecules (alpha and beta forms). The $\alpha$ form is more stable kinetically, being the major form present when the material is subjected to faster cooling rates. The beta form is more thermodynamically stable and benefits from slower cooling rates. The temperature being higher for longer period of time allows an extended time to the building blocks of the vegetable oils (i.e. triacylglycerols) to rearrange themselves in a crystal lattice since beta form is formed from existing alpha crystals (Metin and Hartel, 2005; Ravotti *et al.*, 2020). The main phase transition peak is wider for the 0.2 °C min$^{-1}$ condition which indicates a greater potential for latent heat energy storage (Fig.6). Moreover, only one of the conditions tested (0.2 °C min$^{-1}$) was able to allow stable crystal formation.

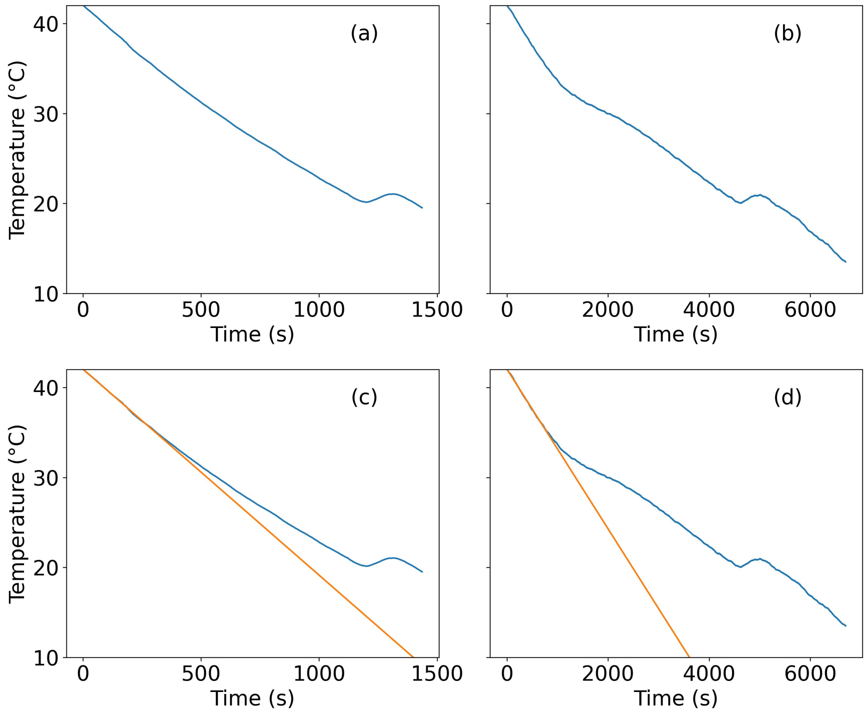


Figure 4. Temperature vs time profile obtained with T-history methodology considering a cooling rate of 0.2 C $min^{-1}$

To evaluate the stability of thermophysical properties, the coconut oil was submitted to nine heating/cooling consecutive cycles during a period of 24 hours (Fig. 5). The cooling condition imposed was (0.2 °C min$^{-1}$). The temperature of the samples is heated to 45 °C and than let cool to reach 15 °C when the cycle is repeated. As can be seen both phase transition region remain within the same temperature interval throughout the whole experiments. This means that the thermophysical properties do not degrade within the time and that the properties will not change if the same condition is applied repeatedly. The result is in accordance with literature since the coconut oil presents a stable phase transition region (Kahwaji and White, 2019).

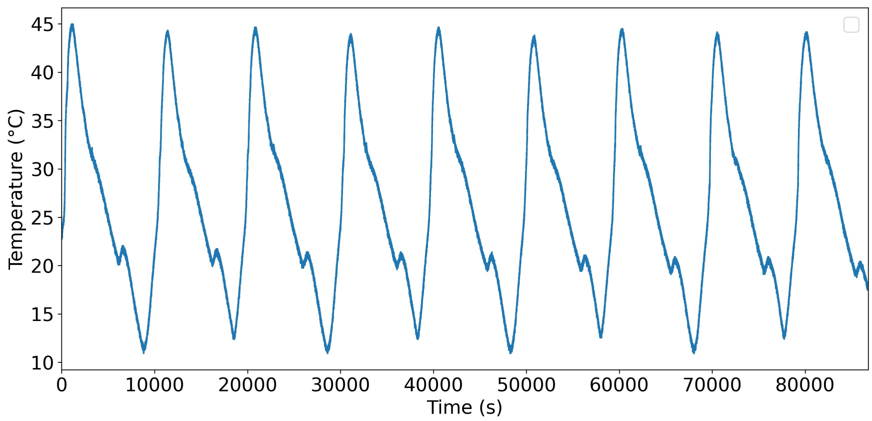


Figure 5. Temperature vs time profile of coconut oil when submitted to consecutive heating/cooling cycles for a period of 24 hours

Moreover multiple phase transition regions can enhance the applicability of coconut oi. Considering the temperature distribution in different Brazilian cities (Fig.7) each one presents a characteristic temperature variation throughout the day. In terms of average temperature of the first semester, Brasilia for example presents a temperature amplitude from 6 p.m. to 9 a.m, variation of around 8 °C in this 16 hour span (rate of 0.008 °C min$^{-1}$) meanwhile Manaus present a variation of around 5 °C within the same period (rate of 0.005 °C min$^{-1}$). This result indicates that the presence of multiple phase transition regions, the material could be partitioned in such a way to obtain just most important peak for each application, e.g. the same coconut oil but will different triacylglycerol composition.

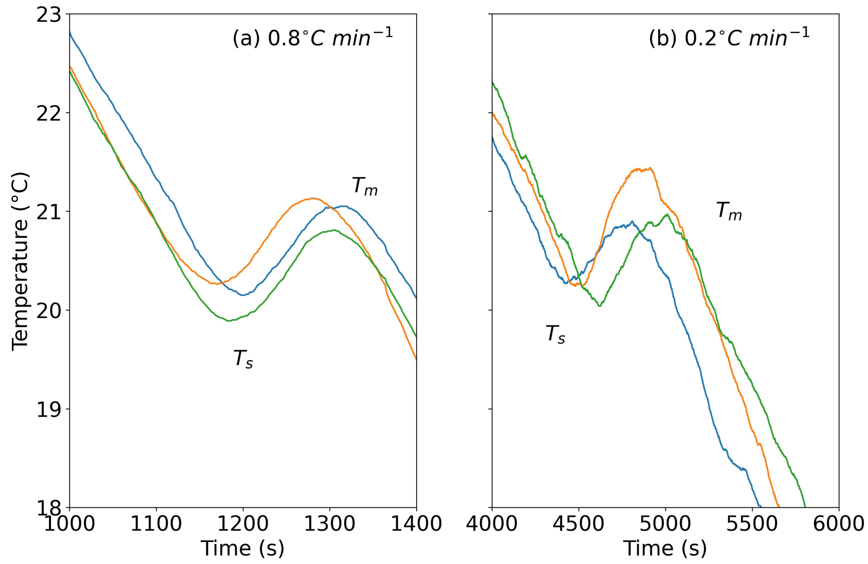


Figure 6. Main phase transition region for coconut oil considering a cooling rate of (a) 0.8 C $min^{-1}$ and (b) 0.2 C $min^{-1}$

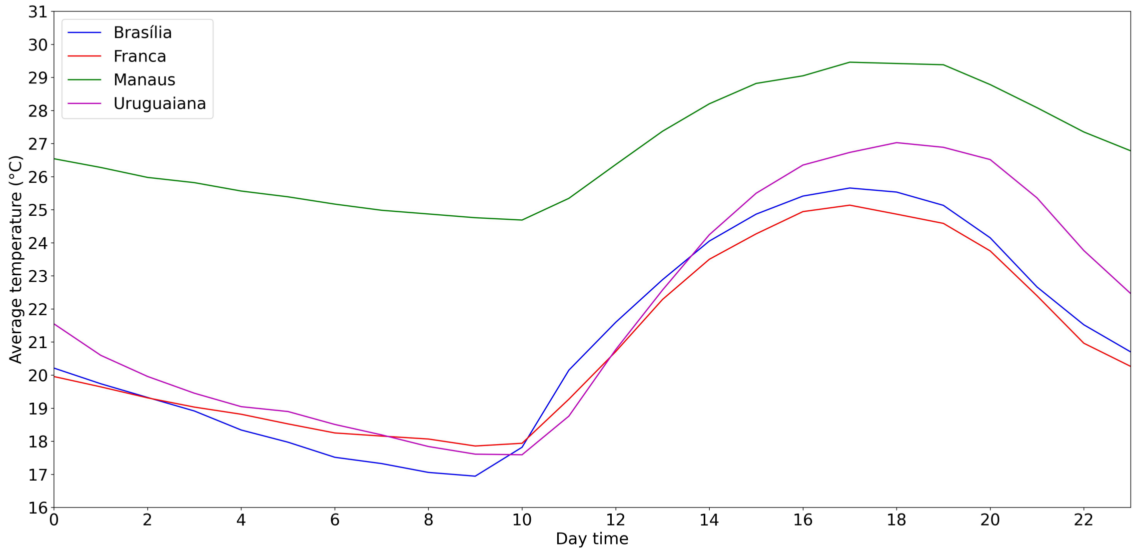


Figure 7. Average temperature variation throughout the dat in differet Brazilian cities

## 4. CONCLUSION

The T-history methodology was applied to investigate the thermophysical of coconut oil as PCM. The methodology was applied to a n-eicosane to validate the experimental setup proposed and the results obtained were coherent with data reported in the literature. Moreover, coconut oil was submitted two different cooling rates when it was observed that slower cooling rates enhance the capacity of the material to store energy. These slower cooling rates allow the material to form more stable crystals which enhance the capacity of the material to store energy. Moreover, it was observed that when coconut oil was submitted to the cooling rate of 0.2 $°C min^{-1}$ the material presents a main peak around 20 °C. Due to its composition, coconut oil could present multiple phase transition behavior which can broaden the applicability coconut oil. This can be done with by oil fraction. This would enrich the mass fraction of the components that release latent in the region of interest.

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