Molecular Catalysis 444 (2018) 76–83

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Research paper

Combining biocatalysts to achieve new phase change materials. Application to non-edible animal fat

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ARTICLE INFO

Article history:
Received 31 July 2017
Received in revised form 30 October 2017
Accepted 31 October 2017
Available online 1 November 2017

Keywords:
Bioeconomy
Bio-based PCM
threo-9
10-Dihydroxystearic acid synthesis
α-Limonene
Fatty acids

ABSTRACT

The thermal properties of various alkyl *threo*-9, 10-dihydroxystearates (DHSEs) prepared from non-edible fat were studied. Non-edible animal fat was hydrolyzed in a 93% yield with *R. oryzae* resting cells. Crude unsaturated fatty acids were recovered from the matter liquor resulting from a crystallization performed to achieve the saturated fatty acids. These unsaturated free fatty acids were epoxidized with 30% H_2O_2 using immobilized *Candida antarctica* Lipase-B (CAL-B) as biocatalyst. The epoxy ring was cleaved with hot water in the presence of *tert*-butanol (*t*-BuOH). Pure *threo*-9, 10-dihydroxystearic acid (DHSA) from animal fat was recovered by crystallization (51% yield). Subsequently, DHSA was esterified in α-limonene using biocatalysts yielding twelve DHSEs (58–90% yield). Differential scanning calorimetry (DSC) analysis of these esters revealed potential latent heats ranging from 136.83 kJ kg^{-1} to 234.22 kJ kg^{-1} and melting temperatures from 52.45 °C to 76.88 °C. Finally, the compounds with enthalpies above 200 kJ kg^{-1} were subjected to 100 and 1000 thermal cycles. These experiments showed that these products present good thermal reliability.

1. Introduction

It has been estimated that the world population will reach 9.2 billion by 2050 [1]. Such growth will bring with it a significant increase in livestock production and animal by-products. In this regard, by-products account for almost 60% of the body weight of a farm animal, while 20% corresponds to non-edible ones. Furthermore, dead and fallen animals increase the amount of non-edible by-products. In this scenario, the reuse of non-edible by-products gains increasing relevance given the public health concerns associated with the non-utilization of such products [2]. Fatty non-edible animal parts comprise mainly triacylglycerides, which contain saturated and unsaturated fatty acids and glycerol. These fats are an interesting source to prepare biodiesel [3] and recently they have been used to prepare bio-based phase change materials (PCMs) [4].

PCMs have the capacity to store heat energy during the phase-change that occurs during melting and solidification processes. In this regard, fatty acids present high thermal and chemical stability and high heat capacity [5,6]. In addition, fatty acids and their derivatives are an excellent source of renewable materials, providing alternatives to currently predominant PCMs such as paraffin and salts [7,8]. Commercially available fatty acid derivatives have recently been proposed as bio-based organic PCMs. These products result from the partial hydrogenation of soy-wax [9,10] or from the hydrogenation of unsaturated triacylglycerides [11–14]. These approaches allow the substitution of paraffin; however, the use of edible oil raises concerns about the likely surplus of food that might cause starvation, especially in the developing countries [15]. Furthermore, although hydrogenation promotes stability during phase change cycles with no risk of oxidation [12,13], the conversion of unsaturated fatty acids to saturated fatty acids circumvents the opportunity of using them for other potential applications.

The unsaturated moieties in fatty acids play an important role in the synthesis of monomers and polymers. The epoxy fatty acid derivatives produced from unsaturated oils allow the formation of pressure-sensitive adhesives (PSAs) [16,17], rubbers [18],

Abbreviations: *t*-BuOH, *tert*-butanol; CAL-B, *Candida antarctica* lipase-B; DHSA, *threo*-9 10-dihydroxystearic acid; DHSE, *threo*-9 10-dihydroxystearate; DHW, domestic hot water; DSC, differential scanning calorimetry; GC-FID, gas chromatography-flame ionization detector; ^{1}H NMR, proton nuclear magnetic resonance; IWH, industrial waste heat; PCM, phase change material.

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http://dx.doi.org/10.1016/j.mcat.2017.10.037
2468-8231/

coatings[18], polyurethanes [18], and acrylate resins [18]. In addition, oleic acid can be converted to DHSA and cleaved in an oxidative manner to azelaic acid in a green and efficient gold-catalyzed system [19,20]. DHSA has recently been used as starting material for the preparation of lubricants [21], soaps [22], deodorant sticks [22], and shampoos [22]. Nevertheless, common lab-scale syntheses of DHSA from commercial oleic acid usually involve the use of chemicals, including formic acid, NaOH and HCl [23] or $MgSO_4$, Na_2SO_3 and hexane [19]. Additionally, DHSA preparation from palm oil-based oleic acid has recently been patented using conventional chemistry [24] in a moment that palm industry is causing concerns in deforestation and affects in biodiversity [25–27].

Recently, we described a procedure using conventional chemistry to transform non-edible animal fat into palmitic-stearic acid eutectic mixtures and DHSA. These products were also analyzed by DSC analysis with distinct behavior, on the one hand, palmitic-stearic acid eutectic mixtures shown good thermal properties, whereas that DHSA presented low chemical stability, presumably caused by the formation of estolides between the diol and fatty acid moieties [4]. In order to afford PCMs from DHSA, the esterification of DHSA into alkyl *threo*-9, 10-dihydroxystearates (DHSEs) should prevent the estolide formation during DSC analysis. Additionally, fatty acid esters have been widely studied as PCMs [28–33] lowering the corrosive action, bad odor and sublimation showed by fatty acids during heating process. Nevertheless, an acid catalyzed or under vacuum esterification of DHSA could also yield estolides. On the other hand, enzymatic esterifications of DHSA present an excellent selectivity towards DHSEs [34,35].

The aim of the present work was to combine biocatalytic reactions to prepare new PCMs (Fig. 1) from non-edible animal fat. First at all, the epoxidation using immobilized CAL-B in a solvent-free media and the epoxide opening with hot water were studied in commercial oleic acid. Subsequently, the non-edible animal fat was hydrolyzed using a bio-catalytic procedure recently described [36], and the crude free acids were split into saturated and unsaturated fatty acids. The unsaturated fatty acids yielded DHSA in the conditions previously studied with commercial oleic acid. Twelve DHSEs were prepared from DHSA and the corresponding alcohol using immobilized CAL-B as biocatalyst and α-limonene as solvent. DSC was used to test the performance of these esters as PCMs.

2. Materials and methods

2.1. Materials

Methanol (≥99.9%), 1-butanol (≥99.5%), 1-dodecanol (98%), 1-hexanol (98%), and oleic acid (90%) were purchased from Sigma-Aldrich Corp. (St. Louis, USA). Ethanol (≥99.9%) was purchased from Scharlau (Barcelona, Spain). 1-Propanol (≥99.8%), 1-pentanol (99%), 1-decanol (97%), 1-tetradecanol (97%), and 1-hexadecanol (99%) were supplied by Fluka (Buchs, Switzerland). 1-Octadecanol (97%) was purchased from Alfa Aesar (Karlsruhe, Germany). 1-Octanol (99%) was purchased from Acros (New Jersey, USA). Hydrogen peroxide (30%) (w/v) solution was provided by Fischer Scientific UK (Leicester, UK). CO_2 was obtained from Messer Iberica de Gases S.A (Tarragona, Spain). *Rhizopus oryzae* resting cells were prepared as described by Gallart-Sirvent et al. [36]. Immobilized lipase-B from *C. antarctica* (Novozym® 435) was a gift sample from Novozymes A/S (Bagsvaerd, Denmark). α-Limonene was a kind gift from Creaciones Aromaticas Industriales (Sant Quirze

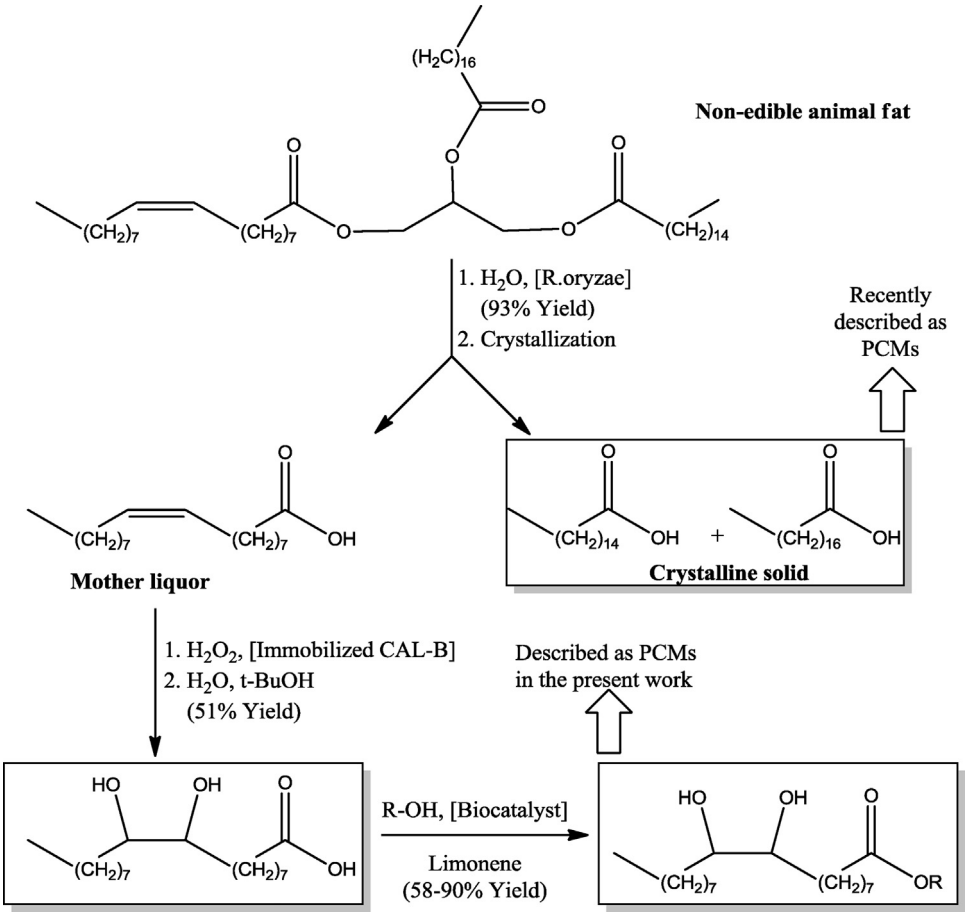

Fig. 1. Syntheses performed in this study. The triacylglyceride structure shows the three main fatty acids present in fat materials.