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Waste oils and their transesterification products as novel bio-based phase change materials

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Abstract

Phase change materials are able to absorb, store and release thermal energy in form of latent heat during solid/liquid phase transition. They have several applications aimed at reducing energy consumption and promoting the use of renewable energy sources such as solar energy. Oils and their transesterification products are bio-based promising alternatives to conventional inorganic and organic PCMs, thanks to their suitable thermal properties. Their possible applications depend on transition temperatures, influenced by the chain length and degree of saturation of fatty acid residues. Based on their properties, oil- and glycerol-derived PCMs are applicable in air-conditioning systems and for the enhancement of thermal comfort in buildings, whereas ester-derived PCMs can be used for refrigeration applications.

Keywords: phase change materials, chilling, thermal energy storage, oils, esters, glycerol.

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Public Interest Statement

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

1.Introduction

Phase change materials (PCMs) are able to accumulate thermal energy by the high latent heat exchanged during solid-liquid phase change. PCMs absorb heat during melting and release heat during solidification. The feasibility and suitable utilization of PCMs depend on the temperature at which this transition occurs [1]. Particularly, they are used in commercial/domestic refrigeration applications when melting temperature is between -20°C and 5°C, in buildings cooling/heating when melting temperature is in the range of 5-20 °C, in heating (solar heating, hot water, electronics applications) when melting temperature is between 40 °C and 80 °C, and in absorption cooling waste heat recovery electricity generation when melting temperature is higher than 80 °C (Figure 1).

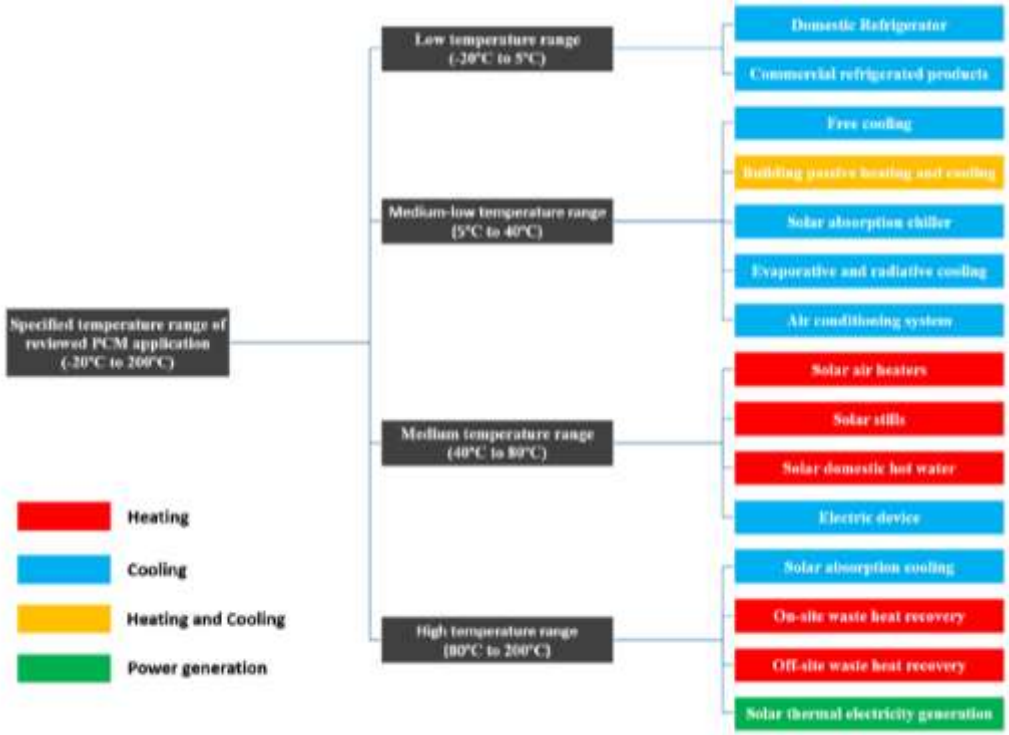

Figure 1. Application of PCMs at different temperature ranges [2].

Beyond appropriate melting temperature and high latent heat, a material should have other suitable thermal, physical, kinetic and chemical properties to be used as a PCM [3]. Among thermal properties, a PCM should have high specific heat for additional sensible heat storage, and high thermal conductivity both in liquid and solid phase to enhance heat transfer. With regard to physical properties, PCMs need favorable phase equilibrium, high density, small volume changes during phase transition and low vapor pressure. Suitable kinetic properties are little or no super-cooling during freezing, high rates of nucleation and crystal growth and effective heat transfer. From a chemical point of view, a good PCM should not be toxic, polluting, flammable, explosive, corrosive and degradable after several freeze/melt cycles. Finally, preferred materials are inexpensive and easy to be recycled and treated.

First materials used were hydrate salts among inorganic PCMs, and paraffins as organic PCMs.

Inorganic PCM are usually non-flammable and have low cost, high melting heat and good thermal conductivity. Nevertheless, they are corrosive, subject to phase separation and super-cooling, and with poor thermal stability. Instead, organic PCMs have lower melting enthalpy and thermal conductivity, but they are stable, non-corrosive and do not show phase separation and super-cooling [4]. Interesting organic PCMs are bio-based materials such as oils, fats and transesterification products. The transesterification of triglycerides with alcohol produces a mixture of esters and glycerol (Figure 2).

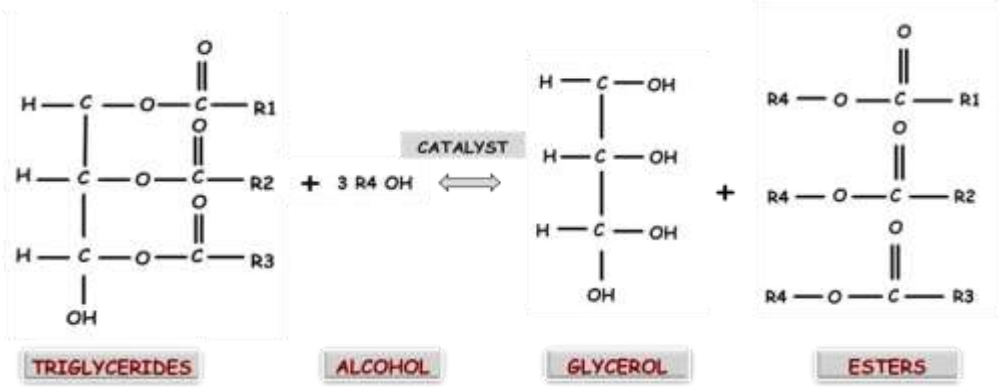

Figure 2. Transesterification of triglycerides to biodiesel (methyl or ethyl-esters mixture) [5].

When these materials are process wastes, they are a sustainable alternative to petrochemical-based organic PCMs [6]. Waste oils are residual cooking oils needing an adequate disposal. Nevertheless, this waste may be a valuable source of energy and material recovery in order to produce biodiesel or other green materials.

This work shows the possible applications of low cost or waste oils and transesterification products as PCMs in chilling and thermal energy storage systems.

2. Applications of oils and transesterification products as PCMs

Applications of oils, esters and glycerol as PCMs include chilling (e.g. air conditioning) and thermal energy storage in buildings.

2.1 Chilling

PCMs applications at low temperatures from -20 °C to 5 °C include domestic and commercial refrigeration. PCMs are used into domestic refrigerators as heat storage on the condenser side and as cold storage on the evaporator compartment. Moreover, PCMs are incorporated into refrigerated trucks, food packaging and medical product, to enhance the thermal buffering capacity and the product thermal protection [2].

2.2 Thermal energy storage in buildings

PCMs applications between 5 °C and 40 °C include free cooling, building passive heating and cooling, evaporative and radiative cooling systems, solar absorption chillers, and air conditioning systems during night. These applications in buildings are very interesting, because they increase thermal comfort, energy savings and efficiency by reducing daily temperature variations and the mismatch between supply and demand of

heat or cold, as well as by regulating room temperature. Such applications require a PCM melting temperature of around 25 °C and plenty commercial availability to be incorporated into building materials. to improve the indoor

3. Use of oils as PCMs

Solid/liquid phase change of oils occurs at low-medium temperatures and strongly depends on fatty acids composition. Generally, the melting temperature increases with increasing chain length and decreasing degree of unsaturation.

3.1 Chilling applications

3.1.1 Non-edible oils

Non-edible oils – derived from seeds of *Calophyllum inophyllum*, *Jatropha curcas L.*, and *Hevea braziliensis* – were investigated as secondary refrigerants in air conditioning chilled water systems [7]. Thermal properties of oils were evaluated by the T-history method [8] and the differential scanning calorimetry (DSC). Results showed melting temperatures between 5 °C and 12 °C, as required for this application [9]. The addition of water and Texapond as a surfactant increased the value of latent heat.

3.1.2 Olive oil

Olive oil is promising as PCM in chilling applications during the pre-cooling step [10]. The phase change temperature and enthalpy of olive oil were determined by the T-history method. Two distinct peaks were observed during both heating and cooling at -4 °C and 10 °C, probably consistent with polymorphism. A slight super-cooling of around 2 °C was observed during freezing. The total melting enthalpy is around 105±11 kJ/kg, slightly higher than freezing enthalpy (97±8 kJ/kg).

3.1.3 Mixture of coconut and soybean oils

The solidification temperatures of coconut oil and soybean oil are around 20 °C and -20 °C, respectively. Therefore, the addition of soybean oil decreases the solidification temperature of the mixture, that is more appropriate for chilling applications. The thermal properties of two mixtures of soybean and coconut oils were determined by the T-history method [11]. Both mixtures showed solidification temperatures between 8.1 °C and 15.9 °C. The mixture with high content of soybean oil (20% in volume) had higher super-cooling (7.8 °C *vs* 3.8 °C), higher melting enthalpy (94.31 kJ/kg *vs* 85.3 kJ/kg), lower specific heat capacity in liquid phase (2.94 kJ/kg K *vs* 6.08 kJ/kg K) and same specific heat capacity in solid phase (2.93-2.94 kJ/kg K).

Many common oils could not be used for thermal energy storage applications due to their low melting temperature, except some saturated-fatty acids rich oils.

3.2 Thermal energy storage applications

3.2.1 Coconut oil

Coconut oil is promising in building temperature regulation as a temperature control agent for room air conditioning systems, thanks to its high content of saturated fat, up to 92% [12], and its melting temperature of 22-27 °C. Its thermal properties were calculated by DSC [12] and T-history method [13], as reported in Table 1.

Table 1. Thermal properties of coconut oil by DSC and T-history method [12,13].

Thermal property	DSC	T-history
Melting enthalpy [Jg^{-1}]	105±11	82±7
Specific heat capacity (solid) [$JK^{-1}g^{-1}$]	1.6±0.2	3.23±0.07
Specific heat capacity (liquid) [$JK^{-1}g^{-1}$]	2.2±0.2	2.35±0.28

Coconut oil has thermal stability for 200 cycles at least and low super-cooling degree.

Moreover, thermal performances of coconut oil were investigated in a thermal chamber by simulating daily temperature conditions in Indonesia with different amounts of oil [14]. Around 135-170 kg of coconut oil are required to decrease temperature by 2-2.5 °C in a typical 3*4 m^2-room. Nevertheless, performances depend on analysis cell sizes and are strongly influenced by the low thermal conductivity of coconut oil. The thermal conductivity can be enhanced by the addition of sonicated graphene into coconut oil [15]. The results of this study showed the highest thermal conductivity increase of 69% when 0.3% wt. of graphene was loaded at 20 °C. However, at these conditions, the latent heat decreased by 11%. Higher graphene concentrations did not improve significantly thermal conductivity because of graphene sedimentation.

3.2.2 Palm oil

Palm oil use in food industry was recently reduced as a consequence of scientific findings about its potential damage for human health. Nevertheless, it is can be used as sustainable organic PCM. The DSC and the thermal monitoring procedure showed two distinct melting peaks in the temperature range of 4-31 °C, which guarantee a total melting enthalpy of about 50 kJ/kg [6]. This value has the same order of magnitude of the first developed PCMs. Degradation kinetics revealed a good thermal stability in medium-low temperatures. Results of life cycle analysis showed that expired palm oil is a very promising alternative to petrochemical-derived organic PCMs.

3.2.3 Tropical plants-derived oils

Oils from tropical plants, such as Allanblackia, shea butter and palm kernel oils, were investigated as novel organic PCMs for thermal energy storage [16]. Their physico-chemical properties were evaluated by DSC, thermo-gravimetric analysis (TGA) and Fourier Transform Infrared (FTIR) spectroscopy. DSC was used to determine whether the energy absorbed or released by the oils was high enough to be used for thermal energy storage and the thermal reliability of the PCM. DSC results showed that all the oils exhibited multiple melting/freezing profile over a wide range, due to their polymorphism. Shea butter and palm kernel oils can not be considered good PCMs, but Allanblackia oil is interesting thanks to high latent heat of energy (80.53 J/g) and the highest melting point

profile (34.74 °C). TGA revealed that all the oils were thermally stable and did not degrade within the temperature of interest, but oxidative instability was observed for Allanblackia oil at around 37 °C. Chemical stability was confirmed by FTIR spectra, used to characterize the functional groups of the oils before and after thermal cycles.

3.2.4 Margarine and shortening

Margarine and vegetable shortening were tested as PCMs, but they resulted unsuitable. Their thermal properties and stability were evaluated by DSC and temperature-versus-time cooling curves. These analyses showed very low melting enthalpy (10 J/g) and high thermal instability since the second heating/cooling cycle [12].

4. Transesterification products: esters and glycerol

4.1 Use of fatty acid esters as PCMs

Esters are promising PCMs, investigated in literature as pure compounds or in aqueous mixture. Ethyl- and methyl-esters are very interesting from an economic point of view, because they can be produced from waste oils by catalyzed (mostly basic) transesterification with ethanol or methanol. Nevertheless, esters can be chemically produced by other routes, such as Fischer esterification, alcoholysis of acyl chlorides and acid anhydrides, etc.

4.1.1 Thermal properties of pure esters

An increasing industrial application of fatty esters is biodiesel, defined as a mixture of mono-alkyl esters from triglycerides. Biodiesel is a green fuel, technically competitive with conventional petro-diesel, but it can give some problems because of nitrogen oxides exhaust emissions, oxidative stability and cold flow. The cold flow is due to the high melting point of saturated fatty esters, cloud and pour points of biodiesel. Chain length, position and configuration of double or triple bonds or functional groups strongly influence the melting and crystallization behavior of fatty acids and esters. The melting point is a crucial physical property determining the suitability of fatty acids and esters in food and non-food applications. Different C_8-C_{24} fatty acids and esters were characterized by differential scanning calorimetry to determine their melting points [17], but results showed discrepancies with other data in literature (Table 2).

Generally, the melting points of the biodiesel fatty esters are high, influencing the cloud point, cold filter plugging point and other cold flow properties [17].

Beyond a suitable melting temperature, a good PCMs should have high melting enthalpy and defined crystallization. The thermal properties of fatty acid derivatives – such as methyl stearate, methyl palmitate, methyl oleate, ethyl stearate, ethyl palmitate and their mixtures – were evaluated by DSC [18]. Their melting enthalpies are around 200 J/g, similar to paraffins. Methyl stearate and methyl palmitate don't show polymorphism. Therefore, they have only one crystallization structure and a defined melting point, so that they are the most promising fatty acid derivatives for PCM applications. Moreover,

methyl palmitate was investigated in a eutectic mixture with lauric acid (40/60%), showing suitable thermal properties in domestic thermal comfort applications (melting temperature of 20-25 °C and melting enthalpy of 205.4 J/g). The mixture was stable for 350 heating/cooling cycles [19].

Table 2. Minimum and maximum melting points (°C) of saturated and unsaturated fatty acids and esters (adapted from [17]).

Chain		Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester	Triacylglycerol
Saturated	8:0	15.4 – 16.5	-40 – -37.27	-44.74 – -43.2	-46.2 – -45	-43.33 – -42.9	9.44
	9:0	11.28 – 15	-35 – -34.99	-44.5 – -36.7	-41.81	-43.1 – -38	9.46
	10:0	30.8 – 31.9	-18 – -13.34	-20.44 – -19.9	-21.84	-22.96	30.37 – 32
	11:0	27.32 – 28.6	-16 – -12.17	-19.43	-19.7	-23.69	27.98 – 31.2
	12:0	43.2 – 44.8	4.3 – 5.2	-15.5 – -1.78	-4.35	-7 – -6.53	46.29 – 46.4
	13:0	41.37 – 45.5	5.17 – 6.5	-4.8 – -2.07		-8.48	44.5 – 44.6
	14:0	53.47 – 58	17.86 – 19.1	11 – 13	9.24 – 10	5.57 – 7	56.5 – 58.5
	15:0	52.15 – 54	18.47 – 19.4	11.5 – 14	11.9 – 12.1	6.26 – 7.1	55.46
	16:0	62.2 – 64	28.48 – 30.5	19.3 – 24.8	20.27 – 21.9	16.07 – 17.1	65.45 – 66.5
	17:0	60.85 – 63	28.58 – 30.2	24.7 – 28	22.32 – 24.7	19.68 – 21	64 – 64.11
	18:0	68.8 – 71.2	37.66 – 39.1	31 – 33.5	28.1 – 31.4	25.63 – 27.5	72.67 – 73.5
	19:0	67.76 – 69.4	38.03 – 41.3	35.28 – 38	32.94 – 33.9	29.2 – 31.4	71 – 71.31
	20:0	73.35 – 77	45.8 – 54.5	40.54 – 50	37.15 – 39	35.14 – 36.8	77.67 – 78
	21:0	73 – 75.2	46.7 – 50	43.66 – 45	42.4 – 43.1	40.1 – 40.4	75.9 – 76.36
	22:0	79.54 – 82	52.2 – 54	47.8 – 50	45.29 – 46.2	43.8 – 44.1	82.5
	23:0	78.74 – 79.6	53.3 – 56	50.8 – 53	48.4 – 49.2	47.3 – 47.5	81.85
	24:0	83.82 – 88	57.8 – 60	54.2 – 57	51.8 – 52.32	50.6 – 50.8	86
Unsaturated	11:1 Δ10	23.91 – 24.5	-27.5 – -24.63	-37.5 – -32.24			
	14:1 Δ9c	-4.5 – -3.91	-52.26	-65.35		-66.19	
	16:1 Δ9c	-1 – 1.22	-34.10 – <15	-36.65 – <15		-52.61	
	16:1 Δ9t	32 – 33	-2.99	-10.99		-12.83	28
	17:1 Δ10c	15.05	-16.02	-20.02		-24.35	
	18:1 Δ6c	28 – 33	-0.97	-7.74			26.24
	18:1 Δ6t	52.38 – 59	19.16	9.45		-11.35	52
	18:1 Δ9c	10 – 16.3	-20.21 – -19.6	<-15		-30.5 – -26.4	-32 – 5
	18:1 Δ9t	43.35 – 45.5	<15	4.17 – 5.8	-12.5	-0.03 – 10.6	
	18:1 Δ11c	12.5 – 15.5	-24.29	-36.49			1.04
	18:1 Δ11t	43.37 – 44.5	9.94	4.10		-0.23	
	18:1 Δ9c,12c	-7.15 – -5	-43.09 – <15	-56.72 – <15		-51.5	-11
	18:1 Δ9c,12c,15c	-11.58 – -11	-45.5 – <15	-61.71	-57.63	-58.61	
	19:1 Δ10c	22.47	-2.33	-7.51			26.12

	20:1 Δ5c	26 – 27	2.39	-8.57			
	20:1 5t	52.5 – 54					
	20:1 Δ8c	35.13	9.11	3.14			
	20:1 Δ9c	23 – 23.5					
	20:1 Δ9t	54					
	20:1 Δ11c	22 – 25	-45 – -7.79	-8.8		-22.69	10.11
	20:1 Δ11t	49 – 54	20.76	14.11			
	21:1 Δ12c	32.96	8.47	5.63			37.97
	22:1 Δ13c	32.18 – 34.7	-3.05	-10.54			29.78 – 32
	22:1 Δ13t	59.16 – 61.9	29.36 – 35	24.5 – 30.5			58
	23:1 Δ14c	43.23	18.22	13.27			
	24:1 Δ15c	39 – 45	9.49	1.21			41.43

4.1.2 Mixture of esters in water

Water is a good PCM, thanks to its low cost, safety, reliability, and suitable thermal properties (specific heat of 334 J/g, melting enthalpy of 297.4 J/g and solidification enthalpy of -102.4 J/g). Nevertheless, water presents high degree of super-cooling during solidification process and cannot be used pure for refrigeration applications at lower temperatures than 0 °C [20]. Therefore, the addition of fatty acids esters in water extends the range of applicability of water-based PCMs to food refrigeration applications.

A mixture of vegetable oil (corn oil and soya oil) esters was added into water at different concentrations (5-12% in volume). Their thermal properties were evaluated by the T-history method [21]. The increase of esters concentration leads to lower melting temperature (from -3 °C to -8.8 °C) and decreasing melting and solidification enthalpy. Moreover, the degree of super-cooling is low, so that the tested mixture can be used as a good PCMs below 0 °C.

A wider range of concentrations (5-35% in volume) were investigated by adding a mixture of corn-oil esters in water [20]). DSC and T-history thermal analysis revealed negligible degree of super-cooling and decreasing freezing temperatures (from -3.5 °C to -27 °C) at increasing concentrations.

Soya oil esters in water (12.5-17.5%) showed similar results, with decreasing freezing point from -6 °C to -9.5 °C. The low super-cooling degree observed is related with the ability of esters to act as nucleant agent, starting crystallization [22].

4.1.3 Other fatty acid esters

Some commercial fatty acid ester-based preparations (Cutina EGMS, Cutina AGS, Cutina CP) are usually used in cosmetic field, but showed interesting melting enthalpies around 200 kJ/kg and potential applications as PCMs at medium-high temperatures (45-60 °C) [23].

Erythritol tetrapalmitate and erythritol tetraestearate were mixed with diatomite and expanded perlite to produce a novel composite PCMs for thermal energy storage in buildings. This material showed a melting enthalpy higher than 100 J/g, chemical stability and thermal stability for 1000 cycles

4.2 Glycerol

Glycerol is a polyalcohol, obtained as a by-product of biodiesel production by transesterification of triglycerides, but also in soap industry, fatty acid industry, fatty ester industry, and from propylene oxide. Its physical and chemical properties (Table 3) make it versatile, biocompatible with other substances, non-toxic, biodegradable and easy to handle [24].

Table 3. Physical and chemical properties of glycerol [24,25].

Properties	Value	
Chemical formula	CH_2OH-$CHOH$-CH_2OH $C_3H_5(OH)_3$	
Molecular mass	92.09382 g·mol^{-1}	
Form and color	Liquid and colorless	
Density	1.261 g·cm^3	
Solubility in 100 parts Water Alcohol Ether	 Infinity Infinity Insoluble	
Viscosity of liquid glycerol At 100% purity At 50% purity	 10 cP 25 cP	
Diffusivity in i-Amyl alcohol Ethanol Water	 0.12·10^{-5} cm^2/s 0.56·10^{-5} cm^2/s 0.94·10^{-5} cm^2/s	
Food energy	4.32 kcal·g^{-1}	
Melting point	17.9-18.2 °C	
Boiling point	290 °C	
Heat of fusion at 18.07 °C	47.49 cal·g^{-1}	
Flash point	160 °C (closed cup)	
Surface tension	64 mN·m^{-1}	
Specific heat in aqueous solution (mol%) 2.12 4.66 11.5 43.9 100	15 °C (cal·g^{-1}·°C^{-1}) 0.961 0.929 0.851 0.670 0.555	30°C (cal·g^{-1}·°C^{-1}) 0.960 0.924 0.841 0.672 0.576

Commercial-grade glycerol with a purity higher than 95% is named ‘glycerine’, while the lower-purity glycerol is termed ‘crude glycerol’ [10]. Thermal and some physical

properties of pure glycerol and crude glycerol were compared in Table 4.

Table 4. Thermal and physical properties of pure glycerol and crude glycerol [26–28].

Material	Melting temperature (°C)	Melting enthalpy ($kJ \cdot kg^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Viscosity (Pa·s)	Density ($kg \cdot m^{-3}$)	pH	Color
Glycerol	18-18.2	~199	0.14, 0.28 (25 °C)	1.41, 1.5	1260 (25 °C), 1261	5.71	Colorless
Crude glycerol	NA	NA	NA	16 (25 °C), 8.46-8.8 (40 °C)	1060 (25 °C)	10.41	Dark brown

The growing biodiesel production caused the increase of glycerol in the global market and the drop of its price (Figure 1), affecting the total biodiesel production cost and its economic viability [29].

It can be chemically converted to esters, ethers, acetals, ketals, diols, epoxides, aldehydes (mostly acrolein [30,31]), ketones, and carboxylic acids, by catalytic hydrolysis, oxidation (also in electrochemical systems [32]), dehydration, acetylation, esterification, transesterification, reforming, pyrolysis, carboxylation, reduction, etherification, ammoxidation, condensation, and acetalization [33–35]. Moreover, glycerol can be biochemically converted to succinic acid, propionic acid, citric acid, lactic acid, ethanol, dihydroxyacetone, propanediol, etc. [36–39], or further used as a carbon source for microbial lipid production [28,40].

The amount and composition of impurities in crude glycerol from triglycerides transesterification depend on the feedstocks and operating conditions during the reaction. They are typically soap, catalyst, unreacted glycerides, glycerol oligomers, polymers, water and biodiesel [40].

These impurities and the high cost of crude glycerol purification – e.g. by chemical treatment, thermal treatment, adsorption on activated carbon, membranes, solvent extraction – make it a by-product of biodiesel industry (around 1 kg of crude glycerol for every 10 kg of biodiesel produced) to be disposed. Nevertheless, it can be a valuable co-product thanks to several applications in different fields [24,33,41].

In addition, glycerol is a new PCM candidate to be used in latent heat storage. Nevertheless, glycerol has a glass transition at -89 °C and its applicability as a PCM is possible only in presence of a fast-crystallization initiation mechanism and if super-cooling and thermally activated change are avoided. The same is true for blends of glycerol and erythritol, a sugar substitute used in food, pharmaceutical and cosmetic applications. Different compositions were investigated and characterized by the T-history method [42,43] to determine the phase change temperatures and enthalpies, but erythritol-glycerol systems did not show any phase change suitable for PCMs [10].

Conclusion

PCMs have a vital role since few decades in efficient latent heat storage applications, as advanced latent heat thermal energy storage materials. Waste oils can be a resource for these novel materials, as well as esters and glycerol.

Waste unsaturated oils could be used as PCMs in chilling, also in suitable mixtures with saturated oils in order to have phase transition at the desired temperature. Waste oils with high saturated fatty acids content, such as coconut oil, are promising in room thermoregulation thanks to their melting temperature of 22-27 °C and good melting/solidification enthalpy. The addition of graphene could increase the low thermal conductivity of oils.

The transesterification of triglycerides is a catalyzed reaction leading to the production of ester mixtures and glycerol. The mixture of esters (generally methyl-esters) is commonly known as biodiesel. Therefore it can be used as biofuel, but also as PCM. Phase transition of esters occurs at low-medium temperatures, so that currently esters have applications in aqueous mixtures. Indeed, water has suitable thermal properties and the addition of esters decreases the melting temperature below 0 °C. Glycerol is emerging as a versatile bio-feedstock for the production of a variety of chemicals, polymers, and fuels. Since it is produced in large quantities during biodiesel production, it can be valorized as co-product for PCMs applications.

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