SUGARCANE WAX EXTRACTION USING HEXANE AND LIMONENE MIXTURES

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Abstract: Hexane is the most widely solvent used in the lipids extraction process, as the case of the sugarcane wax. However, the use of this solvent is highly harmful to the environment, human health, and safety. Limonene is a monoterpene found in the citrus peel, with great potential for employability as a green solvent. In this work, the partial and total substitution of hexane by limonene was carried out in the process of the sugarcane peel wax extraction to evaluate how this substitution impacts the physicochemical characteristics of the wax. The extracted samples were compared with a commercial wax sample (carnauba) from the TGA, DSC, and FTIR analyzes. Through this study, it can be concluded that the waxes obtained from the use of the hexane and limonene mixture solvents, presented similar physicochemical characteristics to those found in commercial waxes, which makes possible the total and/or partial replacement of the hexane by solvents less harmful to health and the environment.

Keywords: sugarcane wax; extraction; solvent mixture; terpenic solvents; green solvents.

INTRODUCTION

Wax extracted from sugarcane peel is a lipidic mixture composed of hydrocarbons, wax esters, sterol esters, ketones, aldehydes and fatty acids and alcohols (Asikin et al., 2012). The characteristics of the wax obtained can vary according to the type of raw material, climatic conditions, extraction temperature and type of solvent used (Georges et al., 2006).

Hexane is generally used as a solvent in lipid extraction processes, such as waxes. However, its use can cause harmful effects due to its high toxicity, flammability, and damage to health and the environment, which makes extra expenses with the security necessary. An alternative that can be proposed is the replacement of hexane by an alternative solvent that is not as harmful to health and the environment, as is the case of limonene. Limonene is a biosolvent extracted from the peel of citrus fruits, which has been tested as a substitute for solvents in oil and lipid extraction processes, showing good results due to its high solvency power. However, limonene is a solvent with a high boiling point (176 °C), which requires a greater amount of energy for its recovery (Mamidipally and Liu, 2004; Virot et al., 2008).

Thus, this project evaluated how the partial and total substitution of hexane for limonene in the process of extracting sugarcane wax influences the physicochemical properties of the obtained waxes.

MATERIALS AND METHODS

Sugarcane peels (variety RB 96 6928) were collected from a sugarcane juice processing farm (Rio Claro, SP, Brazil). The material presents particle size between 0.19 and 0.36 mm, moisture content of 8.0 ± 0.2%, and total lipid content of 7.6 ± 0.5%, determined according to the methodology proposed by Bligh and Dyer (1959).

Extraction and Purification Procedure

The extractions of crude wax were carried out using a Soxhlet apparatus during 1 h, with approximately 10 g of biomass and 200 mL of the mixture by limonene and hexane in different proportions (0, 10, 30, 50, 70 and 100%). The solvents were recovered by evaporation under reduced pressure and dried under ambient conditions.

After drying the crude wax, the sample was purified. For this purpose, it was homogenized in hot hexane (1:20 w/v), cooled to 10 ºC (during 1 h), centrifuged and the hexane was discarded. The extract was then washed with acetone (2:1 v/w) at 10 °C, filtered under reduced pressure, and dried under ambient conditions.

Wax characterization

Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Infrared by Fourier Transform (FTIR) were performed to characterize the obtained waxes. The results obtained were compared with those of the commercial wax from Carnauba (Multiceras - Mexico).

Waxes thermal resistances were measured using a thermogravimetric analyzer TGA-50M (Shimadzu, Japan). About 5 mg of wax was heated from 25 to 600 °C at a rate of 10 °C.min^{-1}, and using a flow rate of 50 mL.min^{-1} of synthetic air. To determine the waxes melting temperatures, a differential exploratory calorimeter (DSC1, Mettler Toledo, Switzerland) was used, with aluminum crucible heating from 25 to 105 °C (at 10 °C.min^{-1}) and cooling to -10 °C (at 10 °C.min^{-1}). After standing for 1 min at -10 °C, the system was reheated to 105 °C (at 10 °C.min^{-1}).

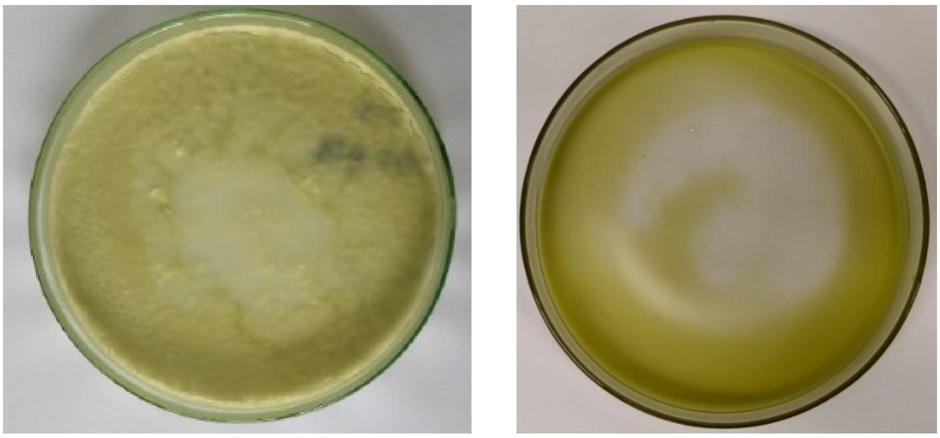
FTIR spectra of the waxes extracts were recorded at 25 °C using a Nicolet 6700 spectrometer (Thermo Scientific, USA) with attenuated total reflectance using Smart Omni Sampler (ATR accessory). The FTIR spectrometer was scanned over the frequency range of 4000-675 cm^{-1} at a resolution of 4 cm^{-1}. The spectrum was collected by using OMNIC 8.0 software.

RESULTS AND DISCUSSION

The visual appearance and texture of the waxes extracted with hexane (or 100% of limonene) and 100% of limonene are presented in Figure 1.

The results of the TGA, DSC, and FTIR analysis are shown in Figure 2.

From the thermogravimetric analysis performed and represented in Figure 2.a, the commercial carnauba wax presents greater thermal stability than the other samples, since its decomposition started around 300 °C, while for the other samples, the decomposition started around the temperature of 200 °C. Upon reaching a temperature of 600 °C, the samples extracted with proportions of limonene greater than 50% did not completely degrade, suggesting that it would be necessary to carry out the analysis at a higher temperature. The sample extracted with 50% of limonene showed the least degradation and loss of mass under these conditions.



(a) (b)

Figure 1. Waxes extracted with (a) 0% of limonene and (b) 100% of limonene.

When analyzing the DSC thermogram (Figure 2.b), melting peak of the wax extracted with hexane (0% of limonene) is more defined and longer than the others extracted with solvents mixtures, indicating that this mixture is more homogeneous in terms of composition than the other waxes. It is also noticed that the melting temperature of the wax extracted only with hexane is 77.81 °C, being closer to the melting point of the commercial carnauba wax, which had a melting point of 82.62 °C.

The FTIR spectra's, Figure 2.c, show that all samples of purified waxes have the same functional groups present in commercial carnauba wax. The bands between 2915 to 2860 cm^{-1} are characteristic of the -CH_2 group and represent the aliphatic fraction of the wax. The bands between 2360 to 2320 cm^{-1} indicates the presence of CO_2 in the air, while the bands between 1715 to 1730 cm^{-1} are characteristic of -C=O stretch, which indicate the presence of esters or fatty acids. The band between 1460 to 1465 cm^{-1} indicates the presence of methylene groups, while the band in 720 cm^{-1} indicates the presence of long or very long chain groups (Athukorala et al., 2009; Qi et al., 2017).

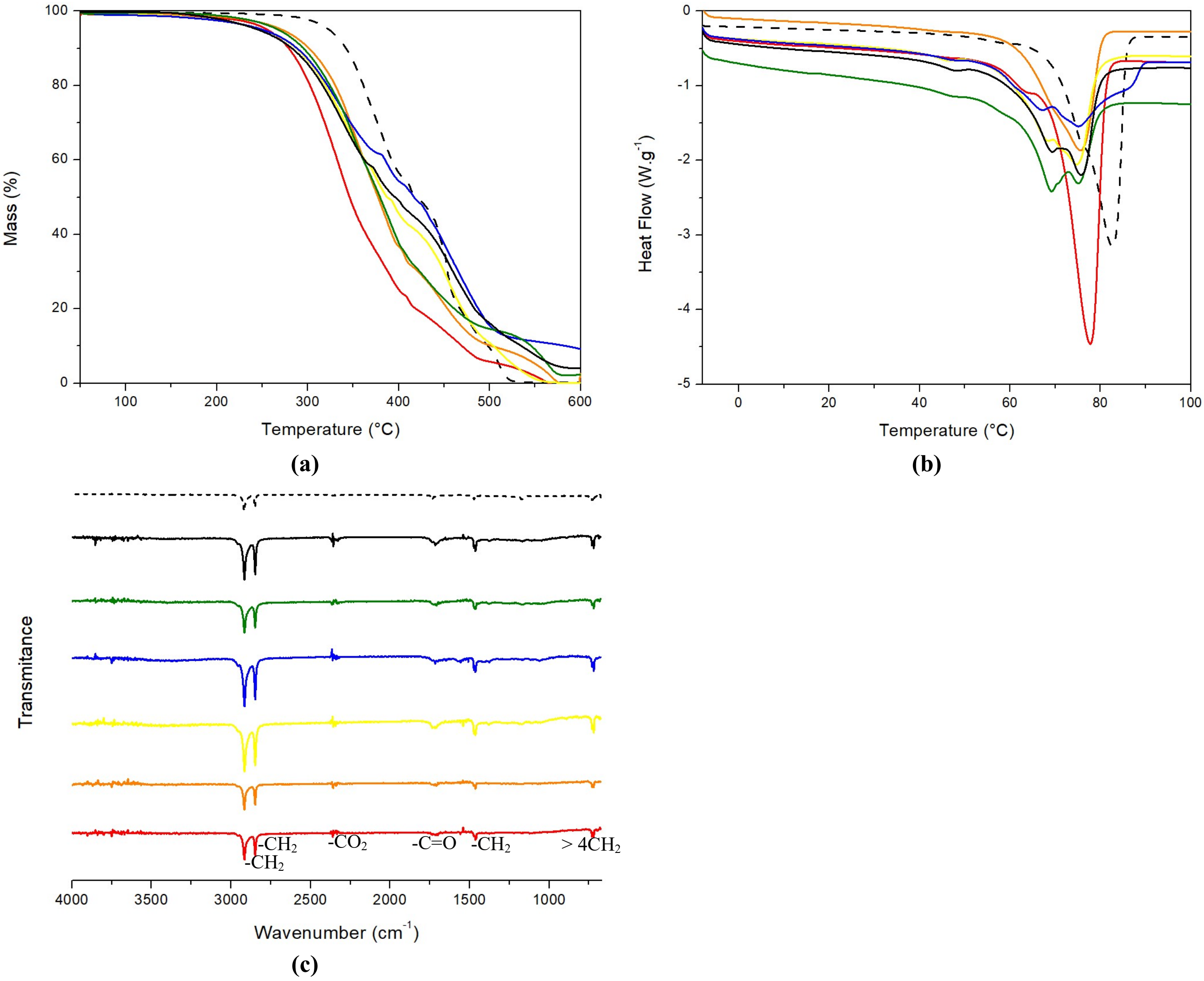


Figure 2. (a)TGA, (b) DSC thermogram and (c) FTIR spectra of carnauba (- -) and purified waxes extracted with 0% (—), 10%, (—), 30% (—), 50% (—), 70% (—), 100% (—) of limonene.

CONCLUSION

In this work, the partial and total substitution of hexane by limonene in sugarcane peel wax extraction was performed to evaluate how this substitution impacts the physicochemical characteristics of the wax. Waxes obtained from mixtures of hexane and limonene solvent showed physical-chemical behavior similar to commercial carnauba wax, thus enabling the total and/or partial replacement of the hexane by solvents less harmful to health and the environment.

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