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Extraction of crambe seed oil using subcritical propane: Kinetics, characterization and modeling

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ABSTRACT

In this study, the extraction of crambe seed oil *Crambe abyssinica* H. FMS Brilhante using subcritical propane as a solvent was investigated. The extraction yield and oil characteristics were compared with the oil extracted using *n*-hexane and dichloromethane. A factorial experimental design was used in order to evaluate the effects of temperature (313–353 K) and pressure (8–16 MPa) on the extracted yield using subcritical propane. It was observed that the temperature has the most significant effect on the extraction yield and the highest yield (32.8 wt%) was obtained at 353 K and 16 MPa. The experimental conditions showed no significant influence on fatty acids composition. Low levels of free fatty acids were found in the extracts (<2%), and the amounts of phytosterols and tocopherols were affected by the subcritical extraction conditions. A longer oxidative induction time was observed for the obtained oil using the subcritical method. The Sovová mathematical model represented satisfactorily the experimental data.

1. Introduction

Crambe (*Crambe abyssinica* Hochst) is an oilseed crop of the Brassicaceae family related to canola and mustard [1,2]. Native to the Mediterranean region, it adapts well to cold and dry climates. The tree can reach 1–2 m in height. The spherical seeds range from 0.8 to 2.6 mm in diameter and have a high oil content of around 38% [3,4]. The seed oil is the main product, and it contains high levels of erucic acid (50–60%), a fatty monounsaturated acid with many applications in the pharmaceutical, cosmetic, lubricant and plastic industries, among others [5].

This oilseed was introduced in Brazil in 1995 by Fundação MS in Maracajú, Mato Grosso do Sul State, where it was identified as a promising crop for biodiesel production. In 2007, the FMS Brilhante variety was registered, with an initial production of between 1000 and 1500 kg ha^{-1} [5]. By 2010, production yields of up to 2300 kg ha^{-1} had been registered [6].

For oil extraction, the methods commonly used are press extraction and solvent extraction. Both methods involve a long extraction period followed by further steps required to separate the oil and solvent. In this regard, the use of pressurized, supercritical or subcritical fluids is an option for replacing the conventional methods. This technology is considered to be clean because, at the end of the extraction, the solvent is completely removed by system depressurization and can be recovered. Although carbon dioxide is the most commonly used fluid in this kind of extraction, subcritical propane allows high extraction rates when used in processes with vegetable oil [7–11] due to the greater solubility of the triglycerides in this solvent [12]. In addition, it can be used at lower pressures, which is an important advantage in the oil extraction industry.

Few studies on subcritical and supercritical extraction technology for obtaining oil from crambe seeds have been carried out. Onorevoli et al. [13] studied the free fatty acids composition and the yield of crambe oil obtained after 30 min of total extraction using propane at 313 K and 15 MPa. However, no information could be found in the literature regarding the extraction kinetics using subcritical propane and the effects of the temperature and pressure conditions on the chemical composition and extraction yield. Thus, studies need to be carried out on the oxidative stability and antioxidant content of extracts obtained by this method.

In this context, the aim of this study was to analyze subcritical propane as an extraction fluid for obtaining crambe seed oil. The effects of the temperature and pressure on the extraction yield were investigated, and the Sovová model was applied in the mathe-

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matical modeling of the extraction kinetics. In addition, oil samples obtained by the subcritical method and by the Soxhlet extraction using *n*-hexane and dichloromethane as solvents were analyzed and compared in terms of their chemical compositions (fatty acids profile, free glycerol compounds and tocopherols) and oxidative stability.

2. Materials and methods

2.1. Sample preparation

Crambe seeds (*Crambe abyssinica* H.) of FMS Brilhante variety (Fundação MS, Mato Grosso do Sul State, Brazil) were used in this study. The peeled seeds were crushed and classified using a system of Tyler series (12–32 mesh) sieves. The particles retained on the 14 mesh sieve were used in the experiments. Seed moisture (4.06 ± 0.02 wt%) was obtained by the gravimetric method drying the sample at 378 K until mass was stabilized. The density ($1.120\,g\,cm^{-3}$) was determined by pycnometry using helium gas (Micromeritics, AccuPyc model 1330).

2.2. Reagents and standards

For the conventional extraction method, dichloromethane 99.5% (Vetec) and *n*-hexane 99% (F. Maia) were used. Propane P.A. 95% (Linde Gás) was used in the subcritical extractions. Potassium hydroxide P.A. (Biotec), methanol PA (Vetec) and heptane 99.6% (Merck) were used in the oil derivatization. To determine free glycerol compounds, content *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA), trimethylchlorosilane (TMCS), the internal standards of 5α-cholestane and methyl heptadecanoate (obtained from Sigma–Aldrich) were used in the oil derivatization. For the determination of the tocopherol levels in the extracts, α, γ and δ-tocopherol standards (Sigma–Aldrich), methanol (J.T. Baker, grau HPLC) and ultrapure water (Milli-Q) were used. Nitrogen 99.9% (White Martins) and oxygen 99.9% (Linde Gás) were used in DSC analysis.

2.3. Oil extraction

2.3.1. Soxhlet extractions

The extractions were performed with a Soxhlet extractor (Laborgas) to determine the oil content of the seeds and to compare the characteristics of the oil obtained by this method with those of the oil obtained with subcritical propane. Approximately 10 g of seeds were used in the exhaustive extraction (480 min) with dichloromethane and *n*-hexane at their respective boiling points carried out according to the method described in AOAC 920.39 [14]. The extractions were carried out in triplicate, and the results are reported as mean value ± standard deviation.

2.3.2. Subcritical propane extraction

The experiments were performed in a laboratory scale unit (Fig. 1). The equipment consists of a solvent, a solvent reservoir, a syringe pump (Isco, 500D model) and two thermostatic baths – one (Julabo, F25-ME model) used to cool the fluid in the syringe pump and the other (Quimis, Q214M2 model) to maintain the extractor at the temperature set point, and a stainless steel extractor with 58 cm^3 of capacity (1.95 cm of diameter and 19.4 cm of height).

A 2^2 full factorial experimental design with center points was used to analyze the influence of the independent variables, temperature and pressure on the extraction yield. In each extraction, the vessel was loaded with approximately 30 g of seeds. The experiments were performed in the temperature and pressure ranges of 313–353 K and 8–16 MPa, respectively, with a mass flow rate of $1.6 \times 10^{-3}\,kg\,min^{-1}$. The oil was collected in an amber glass vessel, and its mass was determined at time intervals of 5 (up to 30 min), 10 (30–60 min) and 20 (60–80 min of extraction). The yields were calculated as the ratio of the extracted oil mass to the initial crambe seed mass. StatisticaTM, version 7, software (Statsoft) was used to analyze the experimental data at the 95% confidence level.

2.4. Mathematical modeling

The Sovová model [15] was used to describe the oil extraction kinetic curves with subcritical propane. The analytical solution of Sovová's model is described by Eqs. (1)–(3).

For $t < t_{CER}$:

$$m(t) = \dot{m}_F Y_S t\,[1 - \exp(-Z)] \tag{1}$$

For $t_{CER} \le t \le t_{FER}$:

$$m(t) = \dot{m}_F Y_S \left[t - t_{CER} \exp\left(\frac{ZY_S}{WX_0} \ln\left\{ \frac{1}{1-r}\left(\exp\left(\frac{W\dot{m}_F}{m_s} \right)(t_{CER} - t) - r \right) \right\} - Z \right) \right] \tag{2}$$

For $t > t_{FER}$:

$$m(t) = m_s \left[X_0 - \frac{Y_s}{W} \ln\left\{ 1 + \left(\exp\left(\frac{WX_0}{Y_S} \right) - 1 \right) \exp\left(\frac{W\dot{m}_F}{m_s} \right)(t_{CER} - t)\, r \right\} \right] \tag{3}$$

where:

$$Z = \frac{k_F a m_s \rho_F}{\dot{m}_F \rho_S} \tag{4}$$

$$W = \frac{m_s k_S a}{\dot{m}_F (1 - \epsilon)} \tag{5}$$

$$t_{CER} = \frac{(1-r)\, m_s X_0}{Y_S Z \dot{m}_F} \tag{6}$$

$$t_{FER} = t_{CER} + \frac{m_s}{W\dot{m}_F} \ln\left[r + (1-r) \exp\left(\frac{WX_0}{Y_S} \right) \right] \tag{7}$$

where $\dot{m}_F$ is the solvent mass flow rate ($g\,min^{-1}$), Y_S is the extract solubility in the solvent ($g_{oil}\,g_{propane}{}^{-1}$), t is the extraction time (min), X_0 is the initial oil concentration in the solid matrix ($g_{oil}\,g_{solid}{}^{-1}$), m_S is the solid mass on an oil-free basis (g), r is the easily accessible oil fraction (X_P/X_0), t_{CER} is the end of the first extraction period (min), t_{FER} is the end of the second extraction period (min), $k_F a$ is the solvent phase mass transfer coefficient (min^{-1}), ϵ is the extraction bed porosity, $k_S a$ is the solid phase mass transfer coefficient (min^{-1}), ρ_F is the fluid density ($g\,cm^{-3}$) and ρ_S is the solid density ($g\,cm^{-3}$). Z and W are dimensionless model parameters.

As described by Ribas et al. [16], the parameter r is a constant associated with the crushing and sieving process and is the same for the entire sample. It was adjusted by the "golden-search" method using the following objective function:

$$F = \sum_{i=1}^{n\_exp} \sum_{j=1}^{N} \left(m_{oil_{i,j}}^{Calc} - m_{oil_{i,j}}^{Exp} \right)^2 \tag{8}$$

The parameters Z and W were calculated using the downhill simplex method [17] minimizing the following objective function:

$$F = \sum_{j=1}^{N} \left(m_{oil_j}^{Calc} - m_{oil_j}^{Exp} \right)^2 \tag{9}$$

where $m_{oil,j}^{Calc}$ is the calculated mass of the oil extracted using the Sovová model, $m_{oil,j}^{Exp}$ is the mass of oil obtained experimentally, n_exp is the number of the extraction experiments and N is the number of experimental data points on the kinetic curve.