

Features of mamona oil of cultivar BRS -188 Paraguaçu

Abstract

The objective of this study was to determine the physico-chemical and physical oil from the castor bean cultivar BRS - 188 Paraguaçu. For characterization of the physical and chemical analyses were made of moisture, acidity, peroxide, iodine and saponification. In the physical characterization were made determinations of density, viscosity at -15, -10, -5, 0, 20, 40, 60, 80 ° C and the point of freezing obtained by the curve of freezing temperature of -196 ° C. The water content was found acceptable, the acidity of the commercial classified as type 1, the iodine establish that it as half-dried, the refraction presented their quality, confirmed by the peroxide below the ceiling, presenting its potential for industry of cosmetics. The density and viscosity decreased with the increase in temperature and the freezing point occurred a little over -90 ° C.

Key words: characterization oil; castor bean; *Ricinus Communis*. L

Introduction

The oleaginous mamoneira has a high-value in the industries. The oil extracted from its seeds does not fit for consumption, however, it has a wide concentration in the importance industrial application (AZEVEDO and LIMA, 2001). In view of this wide application, studies on the influence of temperature are crucial to define properties of products. The castor bean oil is considered the most dense and viscous oils of all, because it can be up to ten times more viscous than some oils. The hydroxyl group gives the compound stability and high viscosity, unlike other vegetable oils, which loses at high temperatures (SAVY FILHO et al., 1999).

The castor bean oil solidifies in low temperatures. Its characteristics make it essential on the employment in aviation, because it does not suffer sudden changes in temperature. The knowledge about the time of freezing is of great applicability for projects and sizing of equipments and for optimizing thermal processes (KASAHARA et al., 1986). The objective of this work was to define the physical-

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chemical characteristics and physical of the crude oil of the castor bean cultivar BRS-188 Paraguaçu.

Material and methods

The oil extraction was held in the small plant of the National Center for Cotton Research (EMBRAPA-Cotton), the physico-chemical laboratory at the Faculty of Bromatology Technological of Ceará (FATEC). Seeds from the field of production of Guaranhus, PE harvest in 2005 was used. Seeds were benefited by the method of extraction by cold pressing, with four percolations, get used to this is a hydraulic press adapted manual developed by Embrapa Cotton.

The calculation of income was obtained by the relation between the quantity of seed that entered the press, on gram, and the amount of oil obtained by pressing. After the process of extraction, the crude oil obtained was placed in centrifuge to separate the impurities of it; gum (hydratable phosphatidic), waxes and colloidal substances, then the following variables were analyzed: water content, index of acidity, peroxide index, saponification index and iodine index, according to the methodology of the Adolfo Lutz Institute (1985), the density were measured at temperatures -15, -10, -5, 0, 20, 40, 60 and 80° C by the pycnometer method, obtained with pycnometer of glass of (with) 25 ml. The volume of pycnometer was measured by weight / volume with water and for determining the mass of the sample. The samples were calculated by the ratio between the weight and volume of the sample of pycnometer.

$$\rho = \left(\frac{B - A}{C - A} \right) \rho_{\text{water}}$$

which:

ρ - density (g cm^{-3});

A - mass of pycnometer;

B - mass of pycnometer + sample;

C - mass of pycnometer + distilled water;

ρ_{water} - water density.

For the temperatures 0, -5, -10 and -15°C, the density of the oil was determined by the relation between mass and volume of the sample. It was used a becker of 25 ml which, when used, was washed and dried in an oven at 50 ° C and then it was put 15 ml of sample, weighing it in analytical balance; then it was placed in a freezer and with the help of a thermocouple the temperature was monitored and when the temperature reached the desired temperature, its volume was checked.

The viscosities were determined through the use of one type of beads viscometer B3, instrument equipped with thermometers and a set of spheres of various diameters and materials. The equipment consists of two concentric cylinders on a basis of metal. This set is tilted to 10 of the vertical and has 3 brands, whose measuring distance travelled by the ball is 50 mm between the marks A and B and 100 mm between the marks A and C. The viscosity is measured by time spent on the ball go in the fluid, the interval between the marks ΔL A and C. The fluid (sample) is placed on the internal cylinder, while the outer cylinder circulates the water, which is the liquid that comes from the bath thermally trated, allowing the achievement of desired temperature.

For the temperatures 0, -5, -10 and -15°C, the outer cylinder was filled with ethyl alcohol to 95% AP (0.91). To get those temperatures it was used a freezer with temperature control, in which the viscometer was placed. The readings when the desired temperature was reached by the sample contained in the internal cylinder, left the ball up and if media with a stopwatch, the interval, Δt , spent the ball to go the distance, $L \cdot \Delta$.

For determination of viscosity was applied to Equation 2.

$$\mu = K (\delta_2 - \delta_1) \Delta t \quad (2)$$

Which:

μ = Viscosity, mPa s^{-1}

K = constant of the ball, mPa cm^{-3}

δ_2 = Density of the ball, g cm^{-3}

δ_1 = Density of the sample, g cm^{-3}

Δt = time of fall, s

In order to determine the curves of freezing, the samples were submitted to the desired temperature in the freezing chamber. It was made packages of low-density polyethylene, size of 81.20 cm per of 54.85 cm wide, they were filled with approximately 35 grams of castor bean oil in order to be obtained, when arranged in freezing camera horizontally, in forms similar to a flat plate. The temperature variation was recorded by placing a thermocouple in the geometric center of the samples by submitting the desired temperature (-196 ° C), following up the fall of the thermocouple temperature recorded at intervals of time pre-established, ie, 3 seconds .

The temperature was obtained through immersion plastic packaging deposited in a metal basket in nitrogen to obtain the temperature of -196 ° C, the curves of freezing were adjusted according to the solution of the

equation $\frac{\partial T}{\partial t} = a \frac{\partial^2 T}{\partial x^2}$ to calculate the transfer of heat, under the transient castor bean oil, for the sample whose shape is similar to a flat plate thickness $2L$, at the moment $F_0 = \Delta t L^{-2}$ (time dimensionless called number Fourier), according to Crank (1975) which is given by:

$$\frac{T - T_{\infty}}{T_0 - T_{\infty}} = \sum_{n=1}^{\infty} A_n \text{Exp} (\sigma_n^2 \cdot F_0) \quad (3)$$

Which:

$$\frac{T - T_{\infty}}{T_0 - T_{\infty}} = RT \quad (3a)$$

$$A_n = \frac{2 \cdot \text{sen } \sigma_1}{\sigma_1 + \text{sen } \sigma_1 \cdot \cos \sigma_1} \quad (3b)$$

$$F_0 = (\Delta L^{-2}), \quad (3c)$$

Which:

RT - Ratio of temperature, dimensionless

T - temperature at any moment, °C

T_{∞} - the means of freezing temperature, °C

T_0 - initial temperature of the product, °C

An - Coefficient that depends on the product

σ_n - root transcendental σ

F_0 - Number of Fourier, dimensionless

Δ - thermal diffusivity effective, $\text{mm}^2 \text{s}^{-1}$

L - thickness of the sample of oil / 2, mm

t - time (s)

With the values of the density of castor bean oil at different temperatures (-15, -10, -5, 0, 20, 40, 60 and 80°C) it was made a linear regression. In viscosity, it was used a complete randomized design with 8 treatments, temperatures (-15, -10, 0, 20, 40, 60 and 80°C) with 6 repetitions. The regressions were performed by using the model of power, proposed by Andrade (1930).

In kinetic freezing of oil, it was established relations between the time and reason (purpose), it was used an analysis of non-linear regression, the coefficients were calculated using the program 'Statistica', version 7.0, and to obtain the graphics it was used the Origin program, version 7.0.

Results and discussion

The results obtained an income of 38% on average, 300 ml of oil to each percolation, for each 1 liter of oil there were four percolations. In table 1 there is the summary of statistical analyses of the

physical and chemical characteristics of oil from the castor bean cultivar BRS-188 Paraguaçu.

In case of table 1 it can be seen that the averages, obtained experimentally, for the physical and chemical characteristics are close to those found in the literature or similar to the standard set by the AOCS, quoted by Freire (2001). It can be seen that for all the variables that the experimental precision was good, measured by coefficients of variation obtained.

The water content obtained a percentage of water on average of 0.5%, according to Santos et al. (2001), the oil can be classified as industrial type 1 because it had a level of water within the maximum of 0.5% humidity. The value of acidity was 0.24 mg KOH g^{-1} . According to Angelucci et al. (1987), this oil can be considered of excellent quality, because it presented an index of low acidity and can be classified commercially as oil-type 1. According to Santos et al. (2001), oils with acidity of less than 1% are classified as type 1.

The index of iodine of cultivar was 93.1 g I 100 g^{-1} . According to Chierice (2001), the index of iodine of commercial oil was 86 g I 100 g^{-1} . The average obtained in the oil under study was a little higher than that of literature, but within the range permitted. This can be classified as semi-dry, because it showed an index of iodine between the range of 80 to 140 g I 100 g^{-1} . According to Cecchi (2003), this determination is relevant to the classification of oils and fats and for some types of processing.

In the analysis of the index of saponification, the values obtained were 139 to 148 mg KOH g, however they are in agreement with the literature.

Table 1. Statistical abstract of physical and chemical characteristics of oil from the castor bean cutivar BRS-188 Paraguaçu.

Parameters	Average	D P*	CV(%)	High	Low	Range
Moisture (%)	0.50	0.009	1.88	0.52	0.50	0.02
Acid (mg KOH g^{-1})	0.24	0.008	3.45	0.25	0.23	0.01
Iodine (g I 1000 g^{-1})	93.1	1.99	2.13	95.69	91.08	4.61
Saponification (mg KOH g^{-1})	141.48	3.20	2.26	146.29	139.86	6.43
Peroxide (meq 1000 $^{-1}$)	0.10	-	-	0.10	0.10	0
Refraction	1.477	-	-	1.477	1.477	0

According to Chierice (2001), the castor bean oil has an average of $180 \text{ mg KOH g}^{-1}$. According to Costa et al. (2004), while studying the oil castor bean, it was found a variation of saponification index of 176 to $184 \text{ mg KOH g}^{-1}$. According to the British standard (FREIRE, 2001) the first quality oil must present an index of saponification between 177 to $187 \text{ mg KOH g}^{-1}$, however these values are set for refined oil, which is not the case of oils analyzed in this study.

The result of the index of peroxide was $0.10 \text{ meq } 1000^{-1}$, below the maximum allowed, which according to Malacrida (2003) shall not exceed the value of $10 \text{ meq } 1000^{-1}$ sample. These values indicate a low possibility of oxidative damage.

The index of refraction observed was 1,477 in the temperature of 25°C . In oils, this index is widely used as criteria of quality and identity (CECCHI, 2003). Pons et al. (2005) studying the index of refraction of the castor bean oil to 20°C , obtained from Nativa cultivars, D26, Tarabai and B-9 found the value of 1479 for all samples, value similar to that found in this study.

With the values of the density of castor bean oil at different temperatures ($-15, -10, -5, 0, 20, 40, 60$ and 80°C) it was done a linear regression as presented

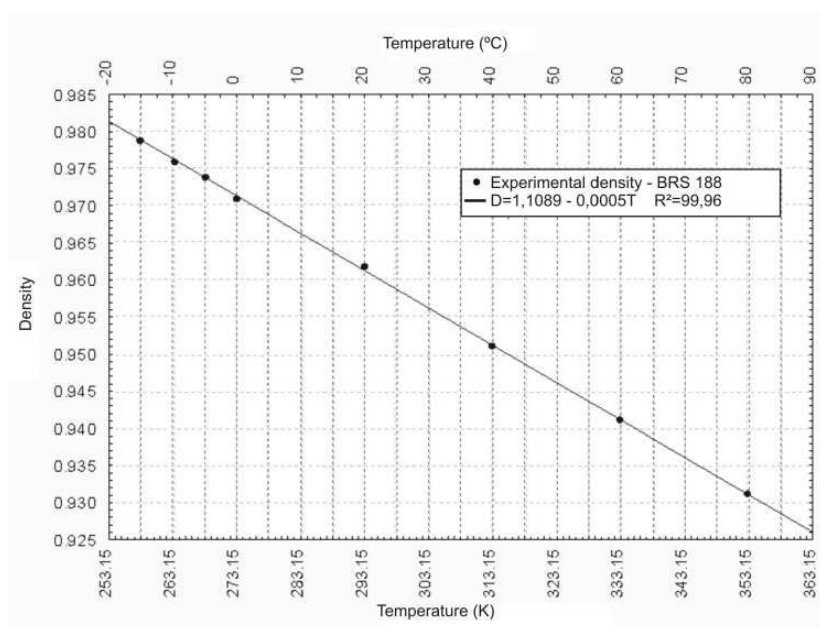
in figure 1. The values of the densities of castor bean oil are in the range from $0,930$ to $0,978 \text{ g cm}^{-3}$ for temperatures ranging from -15°C to 80°C . Observing the curve of figure 1, it can be seen that the density decreases linearly with the increasing temperature, with correlation of over 99%. The behavior decreasing obtained with increasing temperature is typical of Newtonian fluids. According to Castro (1999), similar behavior has also been obtained when it was studied the density of oil of babaçu.

In table 2, there are the results of the analysis of variance performed for the values of viscosity of the oil obtained from the 2 cultivars on 8 temperatures. The analysis of variance resulted in significant differences at the level of 1% compared with the temperatures, cultivars and also for interaction between temperature and cultivar.

In table 3, there is the comparison between the average temperatures in viscosities studied from the cultivar BRS - 188 Paraguaçu obtained on 8 temperatures.

As for the temperature factor, there is a decrease in viscosity of the castor bean oil with increasing of the temperature to 20°C and starting at 40°C to 80°C there is no significant difference.

Figure 1. Oil density from the castor bean cultivar BRS-188 Paraguaçu dependind on the temperature.



This behavior was similar to the oil of both cultivars of castor bean.

Costa Neto et al. (2000) in studies of specifications of some vegetable oils “in nature” found viscosity of $296.87 \text{ mPa s}^{-1}$ for the castor bean oil at a temperature of 37.8°C , comparing with the values obtained in this search in the temperature of 40°C , 194.3 mPa s^{-1} for the BRS-188, it can be said that the values are in agreement, taking into consideration the temperature used in this survey was higher, which leads the viscosity for a lower value. With the data of viscosity of crude oil from the castor bean of cultivar BRS-188 Paraguaçu it was made an analysis of non-linear regression on the model of power, to Newtonian fluids. It was presented by figure 2 that the exponential model proposed by Andrade fits well with the experiments data correlation coefficients greater than 96%.

In figure 3 it is presented the freezing curve of the castor bean oil in the cultivar BRS-188

Paraguaçu at -196°C where it can be seen changes in the behavior of the curve, there is only two phases, the cooling that can be followed until the temperature of -98°C taking until that temperature was reached, 59 and 21 seconds respectively. Although the initial time is very prone to error, since time is measured in intervals of seconds and is difficult to know what time that the sample enter into contact with the nitrogen, and can itself trigger the stopwatch at different times, so it is more reasonable to check the temperature that occurs in the beginning of change that, for both curves, occurred around 0.40; from this point, the process of freezing that is instantaneous is started, that is, it can be seen a decline in the behavior of the curve when a more gentle decrease of temperature begins, which can be identified as the post-freeze phase. There are not three stages well defined, common fact in curves of freezing of biological materials, for the castor bean oil it is only detected a break in continuity of these curves.

Table 2. Analysis of variance of viscosity data from castor bean cultivar BRS-188 Paraguaçu oil.

F.V	G.L	Average square
Temperature (T)	7	210.705**
Residue	40	4.313
CV		0.0443
Total	47	

** = significant level of 1% probability

* = significant level of 5% probability

ns = not significant

Table 3. Average viscosity of the oil obtained from the castor bean cultivar BRS-188 Paraguaçu, at temperatures of -15 , -10 , -5 , 0 , 20 , 40 , 60 and 80°C .

T ^a (°C)	VISCOSITY (mPa S ⁻¹)
-15	16 325.67 a
-10	9 506.50b
-5	7 874.67c
0	4 076.33d
20	992.00e
40	194.3f
60	67.0f
80	25.6f
General average	4 882.7
CV (%)	4.31
DMS	0.388

Note: No statistical differences by Tukey test at 1% probability was observed for averages followed by the same letter

Figure 2. Viscosity of crude oil from the castor bean cultivar BRS-188 Paraguaçu, adjusted using a exponential model for Newtonian fluids, proposed by Andrade, cited by Machado (1996).

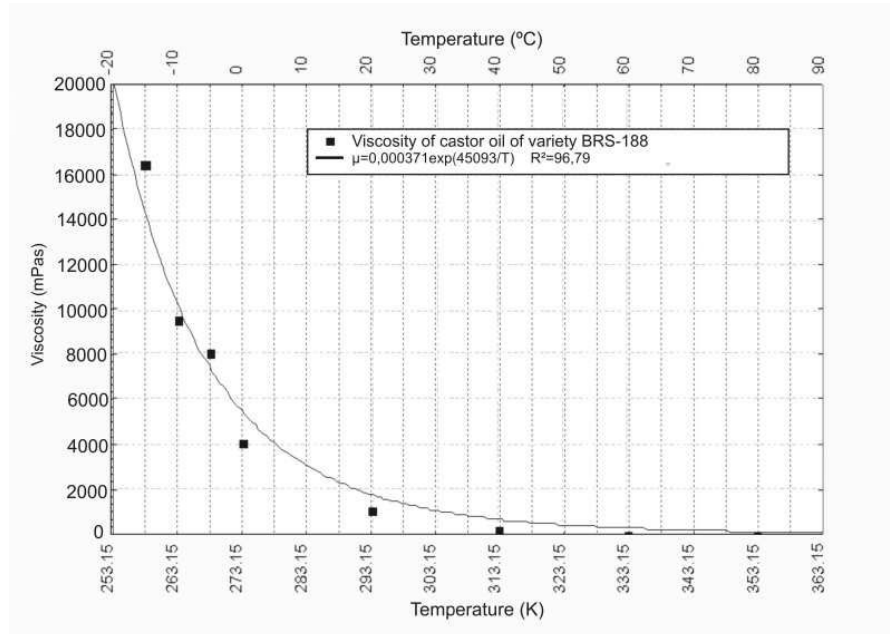
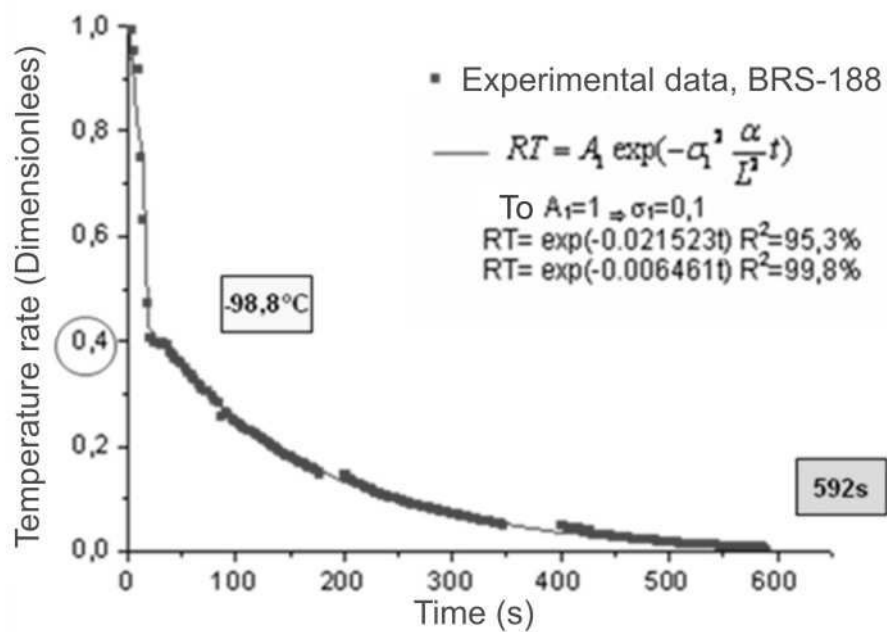


Figure 3. Freezing curves of the castor bean oil cultivar BRS-188 Paraguaçu done at -196°C of temperature.



Conclusion

Based on the results obtained, it was established the following conclusions for the physico-chemical and physical features of the oil from castor bean:

The water content and saponification found in the crude oil from the cultivar studied was an acceptable rate to the castor bean oil; according to the literature the acidity classified as commercial oil of type; the rate of iodine as semi-dry oil and the rates of peroxide and refraction showed its good quality and capability in the cosmetics industry.

The density and viscosity presented a decrease with increasing temperature, the model for exponential Newtonian fluids proposed by Andrade applied to the experimental data in viscosity set up satisfactorily with correlation coefficient higher than 96%, the freezing of the oil was obtained in temperature of -98°C, because from that point the process of freezing instantly began, identified by the collapse of the behavior of the curve, explaining the phenomenon that occurs in the castor bean oil during the reduction of temperature.

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