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Oil extraction from seeds of *Carica papaya* L.: Obtaining the lipid profile and thermal evaluation

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ABSTRACT: Carica papaya L. is frequently found in northern and northeastern Brazil, the Caribbean and Central America. The papaya seed oil was extracted using Soxhlet extraction. Its oil has low acidity, iodine index, saponification and peroxide values adequate and comparable to other commercially available vegetable oils. The lipid profile of this oil was also obtained by gas chromatography; thermal characterization was performed by thermogravimetry (TG) and differential scanning calorimetry (DSC) under various heating rates. The composition of the innature oil indicates that oleic and palmitic fatty acids are predominant. The DSC analysis under cooling shows that the crystallization phase of this oil is similar to olive oil, and the thermogravimetric results show the thermal decomposition under nitrogen purge gas occurs in only one stage. The activation energy was obtained applying the isoconversional methods proposed by Capela and Ribeiro, Ozawa and Friedman. The obtained kinetics data leads to a dependence on the sample mass and purge gases, which results in several kinetic patterns.





1. Introduction

Brazil is the largest producer and exporter of papaya, with the largest plantation being in Espírito Santo state and the northeastern region of the country (Fontes et al., 2012). The papaya belonging to the Caricaceae family, especially the 'Formosa' papaya group, is widely consumed in Brazil. It is a hybrid of Chinese origin, weighing 0.8 to 2.5 kg of yellow or reddish colors, bulky pulp, and sweet with a content of production of more than 70 tons per year (Alobo, 2003). Its seeds correspond to around 14% of fruit in weight and can be used for extraction of oil for pharmaceutical purposes, with 25% of the industrial income (Anuar et al., 2008; Xu et al., 2008). Papaya is an excellent source of β -carotene, ascorbic acid (Alobo, 2003), potassium, other minerals and fibers. In addition, it contains papain, an important enzyme that is an efficient digestive supplement (Monetta, 1987). Papaya seeds, which constitute about 30-35% of the fruit, are generally discarded, both in domestic consumption and in the food industry (Kardash and Tur'yan, 2005). In order to make better efficient use of the fruit, it is worth investigating and using its seeds as a source of oil (Puangsri et al., 2005).

The main purpose of this paper is the extraction, lipid profile by gas chromatography and thermal evaluation of the oil from seeds of papaya (*C. papaya* L.). The thermal study was carried out through differential scanning calorimetry (DSC) and thermogravimetry (TG). In addition, the physic-chemical properties, i.e., acidity, iodine index, saponification and peroxide index of this oil were evaluated.

2. Experimental

2.1 Extraction of the oil and lecithin

After the first attempts at extraction by Soxhlet using hexane as the extracting solvent, the physical-chemical analysis of the oil extracted from the seeds of papaya showed high acid and iodine indexes (Table 1) and rancidity odor characteristics after the storage period. Therefore, some changes were necessary for this first stage of the work, aiming to obtain oil without the presence of lecithin. This was necessary because lecithin has the property of emulsification and antioxidant effects, but its presence in excess can alter the physicalchemical characteristics of the oil (Judde *et al.*, 2003).

Table 1. Indices of acidity, iodine, saponification and peroxide and for different vegetable oils compared to the papaya oil seeds.

Oil	Acidity	Iodine (Wijs)g/100g	Saponification (mg KOH/g oil)	Peroxide (meq of O ₂ /kg oil)
cotton		99-119	189-198	
peanut		80-106	187-196	
canola		110-126	182-193	
sesame	0.3	104-120		
corn		103-128	187–195	< 10
sunflower		120-138		
soybean	2.0	120-143	188–195	
papaya	0.9167	69.13	189.4	2.97
papaya (only hexane)	15.16	153.6		

First, to minimize undesired effects, seeds were seeded from the fruit by hand and then washed and cooked in hot water, at a temperature around 70 °C for 4 h, exchanging water at 1-hintervals, in order to eliminate soluble residues dissolved in the water.

Soon after cooking, the seeds were dried in an oven (Tecnal model TE 394/1) for 8 h at 70 °C and comminuted in a blender to ensure a larger contact surface between the extracting solvent and the particles. Then, the material was properly packed in Soxhlet, using hexane as an extraction solvent. After the extraction with the hexane, a new step of extraction of the oil was carried out, now to obtain the lecithin (Jangle *et al.*, 2013; Patil *et al.*, 2010). The phosphatidylcholine is the main

constituent of lecithin and it was separated from papaya oil by extraction with ethanol. The precipitate formed during the extraction was filtered and the excess ethanol present in the oil was removed by evaporation in a rotary evaporator. The extraction product, assigned as lecithin, corresponds to approximately 3% of papaya seeds.

Natural papaya seed oil was characterized according to analytical indexes for oils and fats. The acid value, which is the amount of KOH (in mg) required to neutralize the free fatty acids in 1 g of oil, was determined according to ASTM 1980-87 (1998).

The iodine index, which represents the measure of the unsaturation of oils and fats, was determined according to ASTM D5554-95 (2011a). Finally, the saponification

index was also determined, according to the methodology described in ASTM D5558-95 (2011b). All titrations were performed in triplicate, and the result is presented as an average of the obtained values.

2.2 Analysis of fatty acid methyl esters (FAME) and thermal analysis

The used methodology to obtain the lipid profile by gas chromatography analysis, described below, follows a pattern of analysis and the description is like that previously published in other works (Kobelnik *et al.*, 2011; 2012; 2014; 2016; 2021; Marques *et al.*, 2015).

The lipid methylation to produce fatty acid methyl esters was done by the method described by Hartman and Lago (1973), with some modifications: sample (30 mg)was diluted in 1.0 mL of *n*-hexane and saponified under boiling with 1.3 mL of 0.5 mol L^{-1} sodium hydroxide (in methanol); after cooling, 1.7 mL of the esterification reagent (ammonium chloride solution in methanol and sulphuric acid) was added and heated to boiling; to the cold solution, 2.0 mL of saturated NaCl solution were added and the top layer was taken for FAME analysis. Fatty acid analysis was performed in a Shimadzu GC 2010 gas chromatograph equipped with a flame ionization detection, under the following conditions: split injection (1:30 injection volume 1 μL); capillary column SP 2560 (Supelco) $(100 \text{ m} \times 0.25 \text{ mm} \times 0.20 \text{ } \mu\text{m});$ injection port and °C detector temperatures and 260 of 250 respectively; initial oven temperature of 140 °C. increasing at 4 °C min⁻¹, to 240 °C, which was maintained for 11 min; and carrier gas of hydrogen at 1.5 mL min⁻¹ flow rate. Identification of the fatty acids was achieved by comparing their retention times with pure standards (FAME 37, code 47885, Sigma Chemical Co.). Data were processed by GC Solution Software, from Shimadzu, Kyoto, Japan. The results were expressed as a percentage of the area of each peak over the total fatty acid profile.

DSC analysis of this oil was carried out from DSC1 Star^e from Mettler Toledo. The mass sample used was around 5.5 mg in the aluminum crucible crimped lids and cooled from 25 to -80 °C and subsequently heated from -80 °C up to 25 °C, both at cooling/heating rates of 1, 2.5, 5, and 10 °C min⁻¹ under nitrogen purge gas at a flow rate of 50 mL min⁻¹.

Simultaneous TG/DTG and DTA curves were performed on a TA Instruments device, model SDT 2960. The conditions used were platinum crucible, purge gases of nitrogen, and synthetic air, with heating up to 500 °C. The kinetic evaluation was performed using the

Friedman Flynn–Wall–Ozawa and Ribeiro–Capela methods, with the DTG curves, which were analyzed in purge gas nitrogen (flow rate from 100 mL min⁻¹), with the heating ratios of 5, 10, 20, and 30 °C min⁻¹ (Dias *et al.*, 2015; 2021; Fonseca *et al.*, 2018; Friedman, 1964; Kobelnik *et al.*, 2018a; b).

3. Results and discussion

3.1 Chemical properties and lipid profile of the oil

The solvent selected for the extraction of oil from papaya seeds was hexane. This choice was based on the ease with which this solvent solubilizes the substance of interest and the ease with which it can be removed from the final product, since it has a low boiling point (69 °C). The total fraction of oil extracted with hexane was approximately 24%.

Chemical properties are among the most important characteristics of oils and fats. The values of acidity, iodine index, saponification index, and peroxide values are chemical properties that are important and show the quality of the oil.

Table 1 summarizes the chemical properties of this oil and the comparison of other commercially available vegetable oils. The acidity index value shows a large difference in the values, which is due to the different ways of extracting the papaya seed oil. The value presented with extraction done only in hexane indicates that the acidity is very high. However, when the seed drying process has changed, the acid number decreases considerably. This new value corresponds to the presence of 1.403 to 1.87% of oleic acid in the oil sample. In the literature, we see that the papaya seed oil extracted with hexane presents 0.33% in oleic acid, as showed by Puangsri et al. (2005), and when papaya seed oil is extracted with petroleum ether, as showed by Von Loesecke and Notle (1937), the acid value is 3.05%. The iodine index obtained before and after the methodology adopted in this work is presented in Table 1, which shows the mass of iodine for each 100 g of oil. The work done by Von Loesecke and Notle (1937) showed that the iodine content had a value of 89.8 g of absorbed iodine per 100 g of oil, which is a value much closer to the value obtained after the modifications described by this work. Puangsri et al. (2005) showed that the oil extracted with hexane shows an iodine value equal to 66.0 ± 0.2 g of iodine absorbed per 100 g of oil.

The indicator of the degree of oxidation is called peroxide index, and it shows the amount of sample that oxidizes the potassium iodide. The value obtained was 2.97 meq 1,000 g^{-1} of oil, which is low and indicates a good state of conservation of papaya seed oil.

Finally, the saponification value shows the amount of salt formed from the fatty acids present in the sample. As the saponification index is inversely proportional to the average molecular weight of the fatty acids in the oils (Damodaran *et al.*, 2010) and the lipid profile shows that the results are concordant, it is concluded that the fatty

acids of low molecular weight (palmitic and oleic) are majority in this analyzed oil.

In addition, Table 2 shows a lipid profile comparison of the oil extracted from papaya seeds with other commercial oils. At room temperature, the oil has a yellow color and characteristic odor. Besides, its color is very similar to the color of olive oil. The lipidic profiles obtained of this oil are also shown in Table 2.

Table 2. Fatty acid composition of papaya seed oil, olive, and others edible oils.

Compound/oil	Papaya ⁺	Olive ⁺	Canola	Corn	Sunflower	Peanut	Soybean	
Fatty acid	Percentage							
Butiric/C4:0	0.34 ± 0.02	-	-	-	-	-	-	
Caproic/C6:0	-	0.15 ± 0.03		-	-	-	-	
Palmitic/C16:0	$14.74{\pm}0.04$	10.6 ± 0.03	3.95	10.48	7.15	12.78	10.82	
Estearic/C18:0	$4.87{\pm}0.02$	3.40 ± 0.02	1.52	2.17	3.58	3.30	3.83	
Araquidic/C20:0	0.37 ± 0.01	0.41 ± 0.01	-	-	-	-	-	
Behenic/C22:0	0.24 ± 0.05	0.10 ± 0.01	-	-	-	-	-	
Tricosanoic/C23:0	-	0.25 ± 0.03	-	-	-	-	-	
Lignoceric/C24:0	-	0.05 ± 0.01	-	-	-	-	-	
Palmitoleic/C16:1	-	0.70 ± 0.03	-	-	-	-	-	
Cis-10-heptadecanoic/17:1	-	0.10 ± 0.01	-	-	-	-	-	
Oleic/C18:1 n9	74.2 ± 0.1	78.0 ± 0.03	58.19	25.90	79.71	39.46	22.40	
Cis-11-eicosanoic/20:1	0.34 ± 0.01	0.23 ± 0.01	-	-	-	-	-	
Linoleic/C18:2	4.88 ± 0.01	5.33 ± 0.01	-	_	-	-	-	
Linolenic/C18:3 n3	-	0.65 ± 0.02	-	-	-	-	-	

⁺Mean standard deviation.

Source: Elaborated by the authors using data from Lipp et al. (2001).

The composition of fatty acids shows that papaya oil, like most vegetable oils, is composed mainly of unsaturated fatty acids of long chain (79.39%), but, in the case, approximately 74% is monounsaturated (oleic acid). Moreover, the analysis of commercial extra virgin olive oil showed composition very similar with the oil papaya seed. The other fatty acids that were not identified in this study were not quantified, probably because they were below the limit of detection, or were not present in the papaya species used. In addition, the main edible vegetable oils and respective compositions for comparative purposes are the palmitic, stearic, and oleic acids (Kalayasiri *et al.*, 1996; Su *et al.*, 2014).

3.2 Thermal evaluation

Figures 1 and 2 show, respectively, DSC curves of cooling and heating. The cooling at different heating rates shows that events shift as a function of temperature. Besides, the cooling evaluation shows that there are two main events at all heating rates, where the first occurs between -4 and -10 °C and the second has a variable interval due to the heating rates. The baseline change seen in the first event is attributed to an arrangement

between the molecules present in the oil, which occurs during the transition from liquid to the solid stage. Besides, there is an additional baseline change for heating rate of 10 °C min⁻¹, which is also attributed to an orderly arrangement between molecules during cooling. In addition, this event was not present in the other heating rates, which indicate that this event is dependent on the cooling rate. The second exothermic peak is attributed to the crystallization phase, which occurs in a single stage.

The heating shows that there was an exothermic event (to heating rate of 5 and 10° C min⁻¹), which is similar to the event seen in cooling. This event is attributed to a molecular relaxation of the oil molecules due to heating. After this event, it is seen that the oil has an endothermic peak at heating rates of 2.5, 5 and 10 °C min⁻¹, which was attributed to the melting point of the oil, with peaks around -3 °C for these curves. However, for the heating rate of 1 ° C min⁻¹, it did not present a defined peak, but a sequence of events between -17 and 10 °C. Furthermore, the heating of 2.5 and 5 °C C min⁻¹ also presents an event between 1 and 10 °C. In other works, it was also seen that during heating and cooling, multiple events occurred, which are successive reactions that are

attributed to the different fatty acid compositions that do not allow us to observe a typical melting point (Kobelnik *et al.*, 2011; 2012; 2014; 2016; 2021; Marques *et al.*, 2015). So, at a heating rate of 10 °C, which is higher than the others, it is possible to see that only one endothermic reaction occurs because there were overlapping reactions attributed due to the components of the fatty acids in the oil.



Figure 1. DSC curves of papaya oil in nitrogen purge gas (50 mL min⁻¹), under several cooling rates of 1, 2.5, 5 and 10 °C min⁻¹ from 25 to -80 °C, sample mass around 5 mg in aluminum crucible crimped lids, without drilling.



Figure 2. DSC curves of papaya oil in nitrogen purge gas (50 mL min⁻¹), heating rate of 1, 2.5, 5 and 10 °C min⁻¹ from -80 to 25 °C, sample mass around 5 mg in aluminum crucible crimped lids, without drilling.

In addition, a comparison with olive oil was performed. Figure 3 shows that the thermal behavior for

heating and cooling of olive oil is very similar to that of papaya seed oil, which is attributed to a small difference in the composition of both oils. The first thermal event occurs between -6 and -9 °C to papaya oil and -12 and -15 °C to olive oil. The second event is an exothermic peak around -50 °C for both oils, which is attributed to the crystallization phase. Furthermore, it is also possible to see that the differences between both oils during the heating are very small: i) the difference at the first event was 5 °C; and ii) the difference between peaks at the second event (melting point) was 3 °C. Besides, olive oil showed an event between 0 and 7 °C, which was attributed to the overlapping transitions (solid–liquid) due to the melting of fatty acids with a higher melting point.



Figure 3. DSC curves of papaya and olive oil in nitrogen purge gas (50 mL min⁻¹), cooling rate of 10 °C min⁻¹ from 25 to -80 °C, sample mass around 5 mg in aluminum crucible, without drilling.

The thermal behavior of this oil evaluated by thermogravimetry, in nitrogen and synthetic air purge gases are shown in Figs. 4 and 5, respectively.



Figure 4.TG/DTG and DTA curves of papaya seed oil: sample mass around 20 mg, heating rate of 10 $^{\circ}$ C min⁻¹ in nitrogen purge gas (100 mL min⁻¹), in platinum crucible.



Figure 5.TG/DTG and DTA curves of papaya seed oil: sample mass around 20 mg, heating rate of 10 °C min⁻¹ in synthetic air purge gas (100 mL min⁻¹), in platinum crucible.

This oil showed that there was not a variation of mass until the temperature of 315 °C in nitrogen (Fig. 4). The thermal decomposition stage occurs in a single step up to 487 °C (mass loss of 99.35%). At the end of the thermal decomposition in nitrogen purge gas, the presence of carbonaceous residues was not observed because pyrolysis takes place, and, therefore, this reaction generates lighter products, which are easily volatilized. In addition, in Fig. 6 shows TG/DTG curves of the oil in several heating rates, which were used for the kinetic study in the nitrogen purge gas. It can be seen in DTG curves that the thermal decomposition behavior of the oil is homogeneous.



Figure 6.TG/DTG curves of papaya seed oil: sample mass around 20 mg, heating rate of 5, 10 and 20 °C min⁻¹ in nitrogen purge gas (100 mL min⁻¹), in platinum crucible.

The analysis in synthetic air (Fig. 5) shows that the DTG curve had a mass variation between 221 and 285 °C, which is attributed to the smoke point, and correspond to the 3.76% of mass variation. This behavior is very common in many oils, as has been cited in the literature (Fontanari et al., 2018; Freire et al., 2013; Jorge et al., 2005; Kobelnik et al., 2021). Thermal decomposition occurs up to 468 °C with two main intervals between 285-363 °C and 363-472 °C, which shows that there are overlapping reactions during decomposition and had weight loss of 47.75% and 40.78%, respectively. At the end of the thermal decomposition, the presence of carbonaceous residues that corresponds to 7.15% of the initial mass was observed. If oxygen is available during the reaction, the molecules will start to be oxidized due to the low activation energy required for oxidation; therefore, molecular scission occurs and generates different products during this degradation, causing the appearance of residues at the end of the reaction.

The DTA (Fig. 5) shows different events on this curve. From the beginning of the curve to the temperature of 195 °C, there was no reaction attributed to the sample. The peak of the exothermic reaction occurs at 341 °C, which is attributed to oil oxidation. After this peak, in the progress of the thermal decomposition, it is possible to see two stages of mass loss at 350–423 and 423–491 °C. In addition, the analysis in nitrogen purge gas shows an endothermic event due to oil pyrolysis.

Regarding the kinetic study, the average values of the activation energy (E_a) were obtained by Capela–Ribeiro, Flynn–Wall–Ozawa and Friedman methods as aforementioned, and the respective results are shown in Table 3.

Table 3. E_a (kJ mol⁻¹) and correlation coefficient (*r*) for decomposition stage.

Purge gas and sample mass	Nitrogen				
Tomponatura rangas	(5 °C min ⁻¹) 300 – 471 °C				
(DTC ourses)	(10 °C min ⁻¹) 321 – 480 °C				
(DIG curves)	(20 °C min ⁻¹) 345 – 495 °C				
Ozawa method	205.4 ± 0.1				
$*E_a(kJ mol^{-1})$ and (<i>r</i>)	(0.99984)				
Friedman method	211.3 ± 0.2				
* $E_a(kJ mol^{-1})$ and (<i>r</i>)	(0.99448)				
Capela-Ribeiro method	196.6 ± 0.1				
$E_a(kJ mol^{-1})$ and (r) and r	(0.9999)				

Figure 7 depicts the relationship between the dependence of the activation energy (E_a) with the conversion degree (α), which is defined as $\alpha = (m_0-m_i) / (m_0 - m_f)$, where *m* is the initial mass with the subscripts 0; i and f, respectively are, initial and final thermal decomposition stages. The results show the comparison of activation energy vs conversion degree (α) of three kinetic methods under nitrogen purge gas. However, the papaya oil had different thermal decomposition behaviors at different heating rates in synthetic air, as shown in Fig. 8. Therefore, the activation energy data under synthetic air are not shown. This happened because TG/DTG curves are not suitable to obtain an adequate displacement to the kinetic calculation.



Figure 7. Activation energy vs conversion degree under nitrogen purge gas.



Figure 8. TG (A) and DTG (B) curves of papaya seed oil under several heating rates in synthetic air purge gas, with sample mass around 20 mg, heating rate of 5, 10 and 20 $^{\circ}$ C min⁻¹, in platinum crucible.

The analysis under nitrogen purge gas (Fig. 7) showed a similar behavior between the Ozawa and Ribeiro methods, while there was a shift in some points of the kinetic behavior with the analysis by the Friedman method in relation to the other two methods. Furthermore, the correlation coefficient (r), which is a measure of the proximity of the association of the points in curves, allows the correlation obtained from the kinetic curves to be verified. As the correlation coefficient values are close to 1, there are a strong correlation between the obtained data. In addition, the behavior of this oil in the three methods allowed us to see that there was the same tendency to increase the activation energy in the degree of conversion (α). This effect is attributed to the increase in interactions between the fatty acid molecules present in the oil. Thus, even during decomposition, an increase in activation energy means that molecular collisions are not sufficient to decrease activation energy, that is, the thermal decomposition of the oil only advances with increasing

temperature, as observed in TG curves. However, nitrogen also causes influence, given that there is no reaction with fatty acid molecules because it is inert. In previous works, with different oils of vegetable origin, it was observed that there is a tendency to have an increase in the activation energy, whether in nitrogen purge gas (Kobelnik *et al.*, 2011; 2012; 2014; 2016).

4. Conclusions

This work presents the results of the physicalchemical analysis and lipid profile by gas chromatography and thermal properties of papaya seed oil.

The obtained information about lipid profile reveal that this oil has a predominance of unsaturated fatty acids, being oleic acid majority with 74.17% in your composition, while the percentage of saturated was 20.56. This oil showed that has similar characteristics to olive oil, which may be an alternative source for commercialization. Furthermore, the lipid profile showed that there are different types of fatty acids present in the oil. Thus, the results obtained by DSC showed that the mixture of fatty acids present in the oil present different thermal behavior in the different heating-cooling ratios. During the DSC analysis, it was observed that there was the crystallization of the oil during cooling, which can be attributed to fatty acids with a larger molecular structure and with a greater presence (oleic/C18:1 n9) since the molecular arrangement is slower than the smaller molecules. Furthermore, DSC curves allowed to observe that there was a significant difference between the cooling rate of 1 and 5 °C min⁻¹, which was sufficient for alteration between the relative size and sharpness of the peak of the DSC curves.

From TG, it was possible to establish the thermal behavior and kinetics parameters of thermal decomposition of this oil. The kinetic study of this oil using the three calculation methods allowed a better evaluation of the kinetic curves. The data obtained by Friedmann did not show good adherence to the methods of Ozawa and Ribeiro, but this is attributed to differences that occur in the calculation mode proposed by each method, which was not discussed in this work because it was not within its scope.

Authors' contribution

Conceptualization: Fonseca, M.; Kobelnik, M. Data curation: Fonseca, M.; Kobelnik, M. Formal analysis: Ribeiro, C. A.; Crespi, M. S. Funding acquisition: Not applicable. Investigation: Fonseca, M.; Kobelnik, M.; Fontanari, G. G. Methodology: Fonseca, M.; Kobelnik, M.; Fontanari, G. G. Project administration: Ribeiro, C. A.; Crespi, M. S. Resources: Ribeiro, C. A.; Crespi, M. S. Software: Not applicable. Supervision: Ribeiro, C. A.; Crespi, M. S. Validation: Fonseca, M.; Kobelnik, M.; Fontanari, G. G. Visualization: Kobelnik, M.; Ribeiro, C. A.; Fonseca, M. Writing – original draft: Kobelnik, M.; Ribeiro, C. A.; Fonseca, M. Writing - review & editing: Kobelnik, M.; Ribeiro, C. A.: Fonseca, M.: Fontanari, G. G.

Data availability statement

The data will be available upon request

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