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# Physical and chemical characterization of the seeds and oils of three papaya cultivars (*Carica papaya*)

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**ABSTRACT**

*Papaya is one of the world's most widely used fruits. Brazil, which is the second largest papaya producer (with an output of 1,517,696 tons, uses most of its production (86.5%) for internal consumption of fresh fruit pulp, which is well liked by the Brazilian population. However, as with most fruit, the seeds are discarded. Contributing to the search for new alternatives in the food industry, this paper aims to analyze the chemical composition of papaya seeds, their physicochemical characteristics, fatty acids composition, and the oxidative stability of the oils obtained from them. Three (3) papaya cultivars: Sunrise Solo, Golden, and Formosa, grown in the state of Paraíba, in northeastern Brazil, were investigated, looking at possible uses for these inedible residues, which are wasted by the tons.*

**Keywords:** papaya, cultivars, *Carica*, oils.

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## INTRODUCTION

Evaluation of the physical and chemical properties of horticultural waste has been the subject of constant study by researchers with the aim of finding new alternative sources for functional foods, and/or new alternative energy sources. Within this perspective, countries like India and Brazil have great research potential, as the world's largest producers of fruits, especially the papaya crop [1].

According to the FAO (Food and Agriculture Organization, 2013) [1], in 2011, the world's leading papaya producing countries were India, Brazil, Indonesia, the Dominican Republic, Nigeria, and Mexico. Brazil occupies the second position, with an annual output of 1.859.343 tons as compared to 4.457.100 tons for India. However, the yield per hectare of Brazilian production (52T/ha) is higher than that of India (38T/ha), though its harvested area is three times larger than Brazil.

Commercially grown papayas belong to the class Dicotyledoneae; subclass Archichlamydeae; order Violales; suborder Caricaceae; family Caricaceae; and genus *Carica*. The small family Caricaceae is divided into four American and one African genre, with 34 species: *Carica* (21 species), *Cylicomorpha* (2 species), *Horovitzia* (1 species), *Jacaratia* (7 species), and *Jarilla* (3 species) [2]. In general, depending on the type of fruit, the most exploited papaya cultivars in Brazil are classified into two groups, the Solo, and the Formosa (Taiwan). In the Solo group, the most consumed varieties are Sunrise Solo (Hawaiian papaya), and the Golden variety (a Hawaiian mutation); in the Formosa group, the most consumed variety is Tainung #1 [2].

Certain studies have been published on the chemical composition of the seeds and physicochemical properties of papaya oil [3,4], the oxidative stability of the oil [5], and its biodiesel by-products [6]. However, most studies do not highlight the variety studied, only the group or more generally, the gender and species. The need remains for studies of the physical properties of the seeds, their content, and oil composition in the different cultivars. This data is considered important for calculating the fruit oil (and its by-product biodiesel) yield per seed type, which is necessary for industrial use. This study aims to analyze the physical and chemical properties of the seeds and oil of three cultivars planted in Paraíba, in northeastern Brazil, thus contributing to the existing data for this "waste", disposed by the ton, for possible industrial use.

## EXPERIMENTAL SECTION

*Material*

In this study we used seeds of three papaya cultivars (Formosa, Hawaiian, and Golden) acquired from Santa Teresa Farms, located on the BR (101 Km), Mamanguape, Paraíba State, in June 2009.

*Methods*

*Sample preparation*

Seeds of three varieties were collected from 3 batches of fresh and ripe fruits and washed with water to eliminate the pulp residues. They were then dried in a vacuum oven at a controlled temperature of 56 °C for a period of 24 hours, and then packaged in 250 g polyethylene bags, vacuum sealed, and stored at 5 °C for later analysis.

*Determination of physical composition*

Fifteen fruits obtained from the 3 batches of each cultivar were weighed, the number of seeds per fruit, and the average respective seed weights in groups of one hundred were determined. These data allowed an estimate of seed weight return per kilogram of fruit in each cultivar. Considering that the FAO and the IBGE make no separate accounting for the areas and production of papayas of the Solo and Formosa groups, our calculations of oil yield (kg/ha) were based on the System of Information and Statistics (SIEM), of the General Warehousing Company of São Paulo (CEAGESP). According to SIEM, 57.3% of 2010 sales were of the Solo group (Hawaiian and Golden), and 42.6% of the Formosa group.

*Centesimal chemical composition of the seeds*

The moisture, lipid, protein, crude fiber, and ash were determined by the Adolfo Lutz Institute Standards [7]. The total carbohydrate determination was accomplished using differencing.

*Oil extraction*

Oil was extracted from the dried seeds (with residual moisture of around 7%). The extraction was performed in a Soxhlet apparatus with n-hexane organic solvent at a temperature of 68 °C for a period of 6 hours. The solvent was recovered at 45 °C in a rotary vacuum evaporator, and the oil was dried in a water bath at 90 °C for one hour.

*Physical and chemical properties of oil*

Indexes: acidity, saponification, and iodine (according to AOCS Cd 5-40 [8]).

Density was determined in accordance with ASTM D 4052, with a digital hydrometer DA-110, Mettler Toledo.

*Determination of the oils' oxidative stability*

This analysis was done by the classical greenhouse method described by Hill, in 1994 [9]. In this method, 100 g of the oil was maintained at 65 °C in a 10 cm diameter porcelain capsule, with the formation of oxidized compounds, the peroxide value was determined in accordance with the method proposed by AOCS Cd 5- 40 [8], and for periods of 0.5, 15, and 20 days to a constant value or a maximum value of 100 $mEq.Kg^{-1}$ equivalent to the point of induction or the detection start point for formation of volatile compounds (oxidized by the Rancimat method).

*Composition of fatty acids*

The methyl esters were obtained according to the Hartman and Lake method [10], and the composition of the esters was obtained by gas chromatography, coupled to a mass spectrometer Model GC-MS QP 2010 Shimadzu of Durabond, a capillary column with stationary phase DB -5HT (30 m length, 0.319 mm inner diameter, and 0.10µm film thickness, using a temperature range of -60 to 400 °C). The retention time was compared with the authentic methyl esters. The relative percentage determined by gas chromatography for each methyl ester sample was an average of three determinations.

## RESULTS AND DISCUSSION

*Physical and chemical seeds composition*

The physical composition of the three papaya seed varieties is presented in Table 1. The average weight of each seed ranged from a minimum of 12.5 mg (Formosa), to a maximum of 15.9 mg (Golden cultivar) the Hawaiian cultivar had an intermediate value of 13.3 mg. The yield of seeds relative to the weight of the fruit was highest in the Golden cultivar (2.54%), followed by the Hawaiian cultivar (1.43%) and much lower for the Formosa cultivar (0.61%).

The theoretical yield for total oil production in Kg/ha in both Solo and Formosa group cultivars corresponded to 204,99 Kg/ha (Table 2), a lower value than that reported for other oil crops such as soybeans and corn, but quite significant considering that these crops' planted area is significantly greater than that of the papaya crop. The results numerically demonstrate the superiority of the Solo group cultivars (Hawaiian and Golden) relative to the Formosa cultivar, which has a production of 42.6%; the Hawaiian and Golden cultivars together add up to a production of 57.3%.

**Table 1 – Physical Parameters of three papaya cultivars seeds**

| Parameters | Formosa | Hawaiian | Golden |
|---|---|---|---|
| *Fruit (g)* | 1318.16 ± 185.82 | 590.32 ± 9.24 | 391.92 ± 16.24 |
| *Seed / fruit (No.)* | 637.06 ± 16.32 | 638.30 ± 18.99 | 623.60 ± 22.81 |
| *Seed / kg / fruit (No.)* | 483.29 ± 0.22 | 1081.33 ± 0.34 | 1591.14 ± 0.34 |
| *Seed / fruit (g)* | 7.99 | 8.46 | 9.95 |
| *Seed yield / kg / fruit (%)* | 0.61 | 1.43 | 2.54 |

*The results represent the mean of 15 determinations*

**Table 2 - Theoretical oil yield (Kg/ha) for the three papaya cultivars**
**Cultivating annual production (Kg/ha) (%) relative to total production Seed (Kg/ha) Oil (Kg/ha)**

| Cultivar | Annual Production (Kg/ha) | (%) in relation to total production | Seed (Kg/ha) | Oil (Kg/ha) |
|---|---|---|---|---|
| Formosa | 22.100 | 42.6 | 134.81 | 37.75 |
| Σ Hawaiian and Golden | 29.900 | 57.3 | 598.00 | 167.44 |
| **Total** | 52.000 | 100 | 732.81 | 204.99 |

The calculation of the seed/ha yield of the Solo group was conducted with the average Σ yield seeds per fruit of each cultivar. The centesimal chemical composition of the seeds of the three cultivars is shown in Table 3 below.

**Table 3 - Chemical seed composition of three varieties of papaya**

| Feature | Formosa | Hawaiian | Golden |
|---|---|---|---|
| *Moisture* | 7.8 ± 0.1 | 6.88 ± 0.1 | 6.5 ± 0.1 |
| *Proteins* | 23.58 ± 1.13 | 24.66 ± 0.49 | 25.45 ± 2.02 |
| *Lipids* | 28.08 ± 2.01 | 28.04 ± 1.42 | 28.03 ± 2.02 |
| *Ash* | 5.12 ± 0.53 | 6.48 ± 0.2 | 5.40 ± 1.59 |
| *Fiber* | 19.19 ± 2.47 | 16.07 ± 0.83 | 16.24 ± 0.58 |
| *Sugars* | 16.14 | 17.8 | 18.36 |

***Note**: Sugars determined by differencing*

The chemical composition (percentages) of the seeds of the three cultivars revealed high levels of lipids and proteins, with fiber, ash, and carbohydrates. The results, in regard to the percentage determinations of lipids and proteins are in agreement with the data presented in the literature by Jorge and Malacrida [5] for papaya seeds of both Formosa and Solo groups, which were respectively (27.5 ± 1.1) and (25.8 ± 1.6) for lipid content, and (25.3 ± 0.9) and (26.6 ± 0.1) for protein content in the respective groups. The Hawaiian cultivar had a higher average ash content (6.8 ± 0.2), followed, in descending order, by the Golden (5.40 ± 1.59) and Formosa (5.12 ± 0.53) cultivars. The ash contents of the Solo groups: Golden and Hawaiian, and the Formosa group cultivars were lower than the values reported in the literature by Jorge and Malacrida [5] for the chemical composition of the seeds, being (7.5 ± 0.0%) and (7.8 ± 0.1%), respectively.

Analysis of the fiber content showed a very marked variation between the mean values determined for the Hawaiian and Golden cultivars respectively 16.07 ± 0.83 and 16.24 ± 0.58, and the fiber content of the Formosa cultivar presenting a content of 19.19 ± 2.47. These results were lower than the percentage content of fiber in the literature published by George and Malacrida [5] 28.2 ± 1.8 (Formosa group) and 29.9 ± 1.2 (Solo group), respectively, and Silva et al. [11] for the seeds of ripe papaya of an unspecified group (29.89 ± 1.13).

The results of this study show that papaya seeds have high nutritional value, and their flours can be used in the composition of human and/or animal feed in the category of a functional food. In a recent study, Porte et al. [12] analyzed the functional properties of papaya seed meal for production use, and observed a high capacity for water (640.88%), and fat absorption (247.61%), which according to the author and collaborators are functional properties, and technology desirable for use as ingredients in food systems such as soups, meats, and bakery products which require high water and fat absorption values, this makes papaya seed meal a viable and cost effective alternative.

*Physical and chemical properties of the oils*
The oils extracted from three cultivars presented an orange yellow color with the characteristic odor of papaya pulp. The physicochemical properties of their respective oils are described in Table 4.

**Table 4 - Physical and Chemical Characteristics of three papaya cultivar oils**

| Feature | Formosa | Hawaiian | Golden |
|---|---|---|---|
| Specific Gravity /25ºC ($Kg.m^{-3}$) | 900.2 | 909.6 | 908.1 |
| Acid value mg $KOH.g^{-1}$ | 1.03 | 0.98 | 1.0 |
| Saponification mg $KOH.g^{-1}$ | 189.98 | 190.14 | 190.2 |
| Iodine value g $I.100g^{-1}$ | 70.45 | 70.26 | 71.3 |

The oils presented low acid values 0.98 (Hawaiian), 1.0 (Golden) and 1.03 (Formosa), good preservation, and chemical stability. Publications on physicochemical properties of papaya oil reveal variations on these index values with (0.78), (1.1), and (2.53) respectively disclosed by Strocchi et al. [13]; Chan et al [14]; Malacrida et al. [3]. The variations are related to the cleansing, and drying technology, and storage of the seeds. The saponification ratios of the three cultivars showed that the average molecular weight of the total fatty acid triglycerides is high. The results obtained were smaller than disclosed by Winayanuwattikun et al. [15]: (202), and Malacrida et al. [3]: (196.4), but are in agreement with previously published work by Chan et al [14]: (193.4), and Strocchi et al. [13]: (187.2). The differences may be explained by the direct relationship between the saponification index and the acidity of the oil. Even with an equivalent sample weight, when the oil has higher acidity, a lower the number of carbon chain esters result from the respective degradation process, which increases the number of carboxylic groups, and consequently greater consumption of KOH occurs during saponification.

The iodine values expressed in (g I.100-1) oils obtained from the seeds were: 70.45 (Hawaiian), 70.26 (Formosa), and 71.3 (Golden) indicating the absence of high levels of trans fatty acids, very common in polyunsaturated drying oils. These results were lower than those disclosed by Malacrida et al. [3]:(79.95); Winayanuwattikun et al. [15]:(75.60), Chan et al. [14]:(74.77) but very close to that disclosed by Strocchi et al. [13]:(70.4) and Puangsri et al. [16]:(66.0).

*Fatty Acids Composition*
The major fatty acid composition analysis of the three cultivar oils revealed qualitative and quantitative similarities as shown in Table 5

**Table 5 - Composition of fatty acids of three papaya cultivar oils**

| **Saturated Fatty acids** | **Formosa (%)** | **Hawaiian (%)** | **Golden (%)** | **Average (%)** |
|---|---|---|---|---|
| C(14:0) Myristic acid | 0.20 | 0.22 | 0.21 | 0.21 |
| C(16:0) Palmitic acid | 18.2 | 18.95 | 18.89 | 18.68 |
| C(18:0) Stearic Acid | 5.30 | 5.07 | 5.20 | 5.19 |
| C(20:0) Arachidic acid | 0.39 | 0.35 | 0.41 | 0.38 |
| Sum | 24.09 | 24.59 | 24.71 | 24.46 |
| **Unsaturated fatty acids** | **Formosa (%)** | **Hawaiian (%)** | **Golden (%)** | **Average (%)** |
| 9 (C16:1) Palmitoleic acid | 0.23 | 0.32 | 0.29 | 0.28 |
| 9 (C18:1) Oleic acid | 72.04 | 70.13 | 69.78 | 70.65 |
| 9,12 (C18:2) Linoleic acid | 3.23 | 4.65 | 4.84 | 4.24 |
| 11(C20:1) Gadoleic acid | 0.41 | 0.32 | 0.38 | 0.34 |
| Sum | 75.91 | 75.42 | 75.29 | 75.54 |

The oils presented a total of eight fatty acids ranging from 14 to 20 carbons. The main feature of the fatty acid profiles of the three cultivars was the high content of monounsaturated fatty acids, in descending order; 72.69% (Formosa), 70.77% (Hawaiian) and 70.45% (Golden).

Oleic acid (C18: 1) was the principal fatty acid component and represented an average of 93.54% of the unsaturated fatty acid composition in the three cultivars, and 99.1% of the monounsaturated fatty acids with a content of 72.05%, 70.13% and 69.78% respectively for the Formosa, Hawaiian and Golden cultivars. Other monounsaturated fatty acids were identified; palmitoleic acid (C16:1) with respective percentages of (0.23), (0.32), and (0.29), and gadoleic acid (C20:1), with respective percentages of (0.41), (0.38) and (0.32) for the Formosa, Hawaiian and Golden cultivars, respectively. The linoleic acid content (C18:2) represented 5.61% of total fatty acids, and was respectively (4.84%), (4.65%), and (3.25%) for the Golden, Hawaiian and Formosa cultivars.

Linolenic acid (C18:3) identified respectively by Malacrida et al. [3], Winayanuwattikun et al. ([15], Puangsri et al. [16] and Chan et al. [14] in the percentages of (0.22), (0.29), (0.2), and (0.6) was not identified in oils of the cultivars presently studied. The saturated fatty acids, present in higher concentrations were palmitic (C16:0) with percentages of 18.19 (Formosa), 18.89 (Golden) and 18.95 (Hawaiian), and stearic with respectively increasing percentages of (5.07), (5.2), and (5.3) for the Hawaiian, Golden and Formosa cultivars. Arachidic acid (C20:0) was characterized in the following percentages: 0.34 (Hawaiian), 0.39 (Formosa) and 0.41 (Golden). Myristic acid (C14:0) presented an average of 0.21% among the cultivars. Behenic acid (C22:0) reported respectively by Malacrida et al. [3] and Winayanuwattikun et al. [15] in the percentages of (0.23) and (0.07), was not identified in the cultivars studied.

The fatty acid composition of the three cultivars studied qualitatively was similar to that reported by Puangsri et al. [16], differentiated only by the absence of linolenic acid (C18:3) which was described by the author at a percentage of 0.2%. The results of this study showed that the average content of saturated fatty acids for the three cultivars (24.46%) was higher than that described by Puangsri et al [16]: (19.4%) and Winayanuwattikun et al. [15]: (21.56%). The mean palmitic acid content in the three cultivars (18.68%) was higher than that described by Puangsri et al. [16]: (13.9%), but close to that reported by Winayanuwattikun [15]: (17.12%). With respect to the results reported for the content of unsaturated fatty acids; oleic acid (C18:1) showed a percentage ranging from 69.78% to 72.04% among cultivars which is in agreement with the values reported by Malacrida et al. [3]: (71.30%), and Winayanuwattikun et al. [15]: (72.91%) but less than that described by Puangsri et al. [16]: (76.8%). The normal content of saturated fatty acids, low in polyunsaturated fatty acids, and high in monounsaturated content in papaya give the oil an average iodine value of (70.6), lower than soybean oils, corn, canola, and sunflower; respectively 138.70, 120.30, 103.80, and 151.90, according to Winayanuwattikun et al. [15]. These data indicate a greater oxidative stability for papaya oil in relation to the other oils cited, as well as suitable physicochemical properties for use as cooking oil

The oxidative stability of papaya oil was investigated only for the Formosa cultivar considering the qualitative and quantitative similarity among the three cultivars for fatty acids (Table 6).

**Table 6 - Oxidative stability of Formosa papaya oil (65 °C)**

| Time (hours) | IP (mEq.Kg-1) |
|---|---|
| 0 | 1.1 |
| 24 | 1.9 |
| 48 | 7.4 |
| 72 | 12.9 |
| 96 | 23.5 |
| 240 | 28.9 |
| 264 | 28.9 |
| 288 | 34.8 |
| 312 | 34.8 |
| 384 | 40.3 |
| 408 | 40.3 |
| 504 | 47.8 |
| 528 | 47.8 |
| 600 | 47.8 |

According to the results in Table 6, we observe that during the first 24 hours there was no significant increase in peroxide value. The initial period of oxidized compounds formation was perceived by sensory analysis and a sudden increase in peroxide value (induction period) occurring between 48 to 96 hours when the index rose from 7.4 $mEq.Kg^{-1}$ to 23.5 $mEq.Kg^{-1}$. This increase continued up to a period of 504 hours (21 days), when the peroxide value reached 47.8 $mEq.Kg^{-1}$ and remained constant until 600 hours, never reaching 100$mEq.Kg^{-1}$, which is the peroxide index requiring changing of the electric potential of the automated equipment, which is based on measurements of electrical conductivity such as Rancimat, and whose value marks the beginning of the induction period for the formation of volatile compounds (according to DE MAN et al, [17]). After 504 hours of experiment, (much lower than the Rancimat equipment induction time), the stabilization of the peroxide index initiated, at a value of 47.8 $mEq.Kg^{-1}$. The results demonstrate the high thermo-oxidative stability of papaya oils which is related to their normal content of saturated fatty acids (± 24%), and high content of monounsaturated fatty acids, (principally oleic acid at ± 70%). The result is in agreement with O'Keefe et al. [18], where researchers compared the thermos-oxidative stability of peanut oil with a high content of oleic acid (75%), and of linoleic acid (4.7%) as compared to soybean oil that presented in its composition (± 56%) oleic acid and (24%) linoleic acid. The O'Keefe study demonstrated that 5 g of peanut oil at a temperature of 80 °C showed an induction time of 686 hours to reach a peroxide value of 100 $mEq.Kg^{-1}$, the formation point for detection of oxidized compounds using the Rancimat test.

## CONCLUSION

The seeds of the three papaya cultivars presented high amounts of proteins, lipids, fibers and minerals, and as such, through the use of this disposable fruit residue; they are viable as an alternative source for use as either human or low-cost animal food. The contents and the physical-chemical composition of the oils in the three varieties are qualitatively very similar, allowing mixing of the seeds for food and/or energy use. There is no direct relationship of proportionality between the yield of seeds and the weight of the fruit. The highest weight cultivar (Formosa) had the lowest yield; the lowest weight cultivar (Golden) had the highest yield. The average composition of the majority methyl esters in the oils of the three cultivars (oleic acid, palmitic acid, and stearic acid), give the oils excellent physicochemical properties and high oxidative stability.

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