Extraction of Pectin from Epicarp and Mesocarp Fractions of Cocoa Shell

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Cocoa (*Theobroma cacao L.*) is a fruit widely cultivated in the world, mainly because it is the natural material used in the production of chocolate. Cocoa husk corresponds to approximately 80% of the fruit and is the main residue of production involving this fruit. Therefore, studies have been carried out to reuse the cocoa husk, including the extraction of pectin, which is a soluble dietary fiber present in the cell wall of many fruits. The study aimed to extract pectin from the cocoa husk, presenting parameters such as acid concentration, temperature, extraction from other sources. In the study, the yield of pectin extracted from cocoa husk using 0.086% citric acid at 90°C for 60 minutes was 10.75% for the epicarp and 5.75% for the mesocarp. Keywords: Cocoa Husk. Pectin. Soluble Fiber.

Abbreviations: ABIA: Brazilian Food Industry Association; GDP: Gross Domestic Product; C4: carbon 4; C5: carbon 5; IMC: Iquitos Mixed Calabacillo; SHMP: Sodium Hexametaphosphate; BPP: Banana peel pectin; HCl: Chloridric acid.

Introduction

The food industry has a great contribution to the national economy. According to data from the Brazilian Food Industry Association (ABIA) in the 2020 annual balance, the food industry was the sector that obtained 10.6% of the Brazilian Gross Domestic Product (GDP) with investments above 21.2 billion of reais and 64.4% contribution to the country's trade balance [1].

Over the years, the food sector has undergone several changes, one of which is the change in eating habits and the search for healthier and more natural foods [2]. In this scenario, fruits have been the target of several studies and researches to extract nutrients from fruit by-products.

Cocoa is one of the most cultivated fruits in the world. Brazil is one of the largest cocoa producers, occupying the seventh production in the global ranking [3]. In the cocoa industry,

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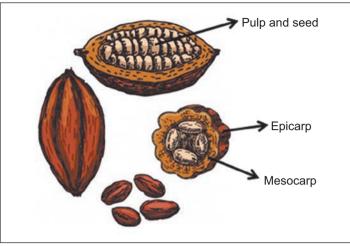
pulps and seeds are the most used part of the fruit and are destined for other related products. Thus, a large residue of the peel, which corresponds to 80% of the fruit, is discarded [4]. Among the possibilities for reusing the cocoa husk, there is the extraction of pectin, which is a dietary fiber present in the cell wall of many fruits and can be widely used in the food industry as an ingredient, acting as a flavor retention agent, as a hydrocolloid acting as a thickener and stabilizer and adding nutritional benefits to the food [5,6].

Cocoa has three important parts: the fruit itself, consisting mainly of pulp and seed. In addition, the fruit has a layer that covers it externally, called the epicarp, and the mesocarp, which is an intermediate layer considered the most developed part of the fruit (Figure 1) [7,8].

The extraction of pectin can be done through an acidic or basic aqueous medium, or by the action of enzymes. Among them, the most used is with the use of acid as an extracting agent, through acidic hydrolysis, where the breakdown of the glycosidic bond between carbons 4 and 5 (C4 and C5) occurs in which the hydrogen in C5, more acidic in the function of the methyl ester group is attacked by the hydroxide ion (Figure 2) [5, 9]. The extraction steps are summarized as obtaining the shell flour, extraction in an acidic medium, and isolation of pectin.

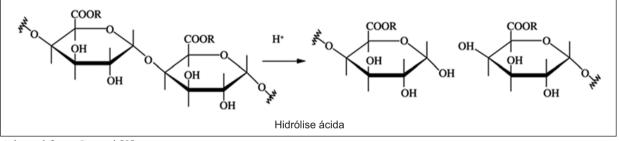
Received on 10 March 2021; revised 15 May 2021. Address for correspondence: Emanuele Santana Bispo dos Santos. Rua Portugal, Nº 48, Zipcode: 41390-080, Salvador, Bahia, Brazil; E-mail: emanuelesant1703@gmail.com. Article selected from VI SENAI CIMATEC Scientific and Technological Research Evaluation Seminar - 2021.

Figure 1. Cocoa parts.



Adapted from Freepik [8].

Figure 2. Pectin acid hydrolysis reaction.



Adapted from Canteri [9].

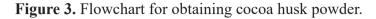
As pectin presents itself as an alternative for adding value to solid waste generated by the cocoa industry, associated with minimizing the volume to be discarded, this work aimed to extract pectin from two different parts of the cocoa husk, epicarp, and mesocarp, through acid hydrolysis, comparing the results obtained.

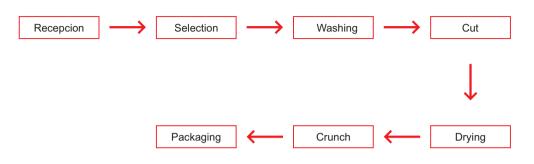
Material and Methods

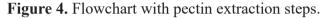
The raw material, object of study of this work, was cocoa (*Theobroma cacao L*.) supplied by the company Mais do Cacau, located in Ilhéus, in the south of Bahia (Brazil). For better pectin extraction efficiency, the cocoa husks were submitted to pre-processing to be transformed into a powder. For this, the fruits were received, selected, sanitized, manually cut to separate the skin from the pulp, the skins were dried in an oven at 50°C and crushed in a mill until the powder was obtained (Figure 3). For the extraction of pectin, the methodology of Canteri (2010) was followed with some adaptations [10]. An extracting agent, citric acid, at a concentration of 0.086% in a 1:50 ratio (solute/solvent) was used. Initially, the shell powder was hydrated with distilled water for 10 minutes with stirring. Then citric acid was added and the solution was heated on a hot plate with stirring until reaching a temperature of 90°C. After reaching the extraction time of 60 minutes, the solution was cooled to 30°C in an ice bath and then filtered using synthetic fabric.

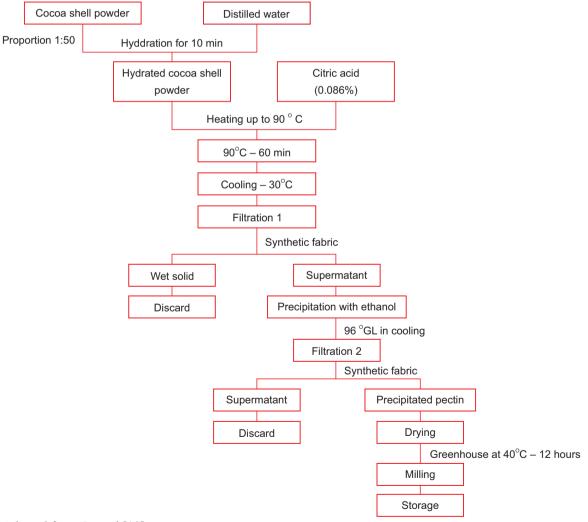
The supernatant was filtered and the wet solid was discarded. Then, pectin was precipitated by adding 96% ethanol (1:2 v/v) to the supernatant for 30 minutes at rest under refrigeration temperature.

After precipitation, the pectin was oven-dried at 40°C for approximately 12 hours for yield calculations. Figure 4 [10] contains the flowchart with the pectin extraction steps.









Adapted from Canteri [10].

Results and Discussion

After the pectin precipitation step (Figure 5), a sample of pectin extracted from the epicarp flour (Figure 6) and cocoa mesocarp, after drying and crushing (Figure 7), was used to calculate the yield (Equation 1). To calculate the pectin yield obtained during the extraction, the following calculation was used:

$Yield = \frac{\text{extracted pectin}}{\text{flour dough (dry)}} x \ 100 \ (1)$

The yield of pectin extracted from the cocoa husk in this work, under the conditions mentioned, was 10.75% for the epicarp and 5.75% for the mesocarp. According to Vriesmann (2012) [11], among the polysaccharides present in cocoa husks, 60% are pectins. The study by Barazarte and colleagues (2008) [12], obtained yields between 2.64 and 4.69% of pectin from the cocoa husk, variety Forastero clone IMC 67, coming from the Caucagua zone in Venezuela, using acid extraction. Partially purified pectins extracted from cocoa husks, according to Arlorio and colleagues (2001), [13] had a yield of $1.29\pm0.08\%$, through the use of sodium hexametaphosphate (SHMP) solution at 75 °C for 60 minutes. In the study by Mollea and colleagues (2008) [14], the authors realized that the amount of pectins is influenced by the extraction time in which when the time goes from 1 to 2 hours, the extracted amount is doubled (2.0% and 4.0%, respectively.

Commercial pectins are generally obtained from citrus fruit peels and pomace or apple pomace, byproducts obtained after juice extraction by industries. Apple pomace contains 10% to 15% pectins and citrus peels contain 20% to 30% pectins [15]. Other sources of pectins have been studied, such as banana, passion fruit, and mango peels. In the research by Maneerat and colleagues (2017) [16]. Banana peel pectin (BPP) was obtained through an aqueous acid extraction with HCl and water for 30 to 12

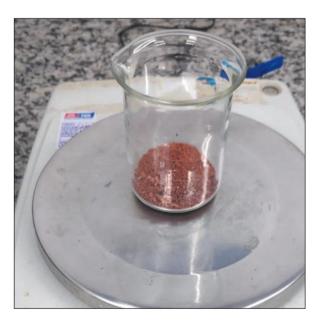
Figure 5. Precipitation of pectin with 96% ethanol.





Figure 6. Pectin obtained from cocoa epicarp flour.

Figure 7. Dry pectin after grinding.



minutes at 90±5 °C and obtained a yield between 7 and 11% of dry basis. In a study with mango, Koubala and colleagues (2008) [17] considered three extraction conditions: HCl, deionized water, and ammonium oxalate and found higher yields with ammonium oxalate and HCl and lower yields with water. According to Canteri (2010) [10], pectins extracted from passion fruit using nitric acid as an extracting agent, the mesocarp fraction

obtained a higher yield with 13.6% of dry base. However, due to the yield and characteristics of the pectins obtained, further studies are needed to improve the properties and yields.

Conclusion

The yield of pectin extracted from cocoa husk in this work showed a satisfactory result when compared to pectin obtained from other sources, thus, the work showed to be very promising. Furthermore, this study contributes to the further characterization of pectin extracted through analysis of the physicochemical properties of soluble dietary fiber.

Acknowledgments

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