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Research Paper

Economic Potential of the Process of Polyphenol Extraction from Cocoa Pod Husk (Theobroma cacao L.) Using the Ultrasonic-Assisted Extraction Method

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Abstract: Polyphenols are phytochemical substances in plants that can work as antioxidants which can inhibit oxidation and the formation of free radicals. Polyphenols can be found in almost all plants, like cocoa pod husk. This research was conducted to determine the feasibility of the polyphenol extraction process from cocoa pod husk using the ultrasonic-assisted extraction method from an economic perspective based on the effect of drying the material and the type of solvent used. The solvents used were distilled water, 96% ethanol and 95% methanol on materials without drying and materials with drying to a water content of ±11%. From the research results, optimum extraction results were obtained for the samples by drying the material and using distilled water solvent at an extraction time of 60 minutes, which produced a yield of 7.95% and a phenolic content of 22.01% or 220.1248 mg gae/g. From an economic perspective, this process provides a profit of IDR 539,683.05/kg. The extract yield and economic benefits obtained from the ultrasonic-assisted extraction method are greater than from the maceration method.

Keywords: Cocoa pod husk; polyphenols; economic potential; ultrasonic-assisted extraction.

1. Introduction

Reactive oxygen species (ROS), commonly known as free radicals, are atoms or molecules that have lost electrons [1]. Free radicals become unstable and can cause cellular or tissue damage when present in excessive amounts [2]. The formation of free radicals is inevitable [3], thus requiring antioxidants that function as inhibitors to slow down the oxidation process of these radicals. One of the natural compounds that can act as an antioxidant is polyphenol. Polyphenols are plant-derived phytochemicals characterized by multiple phenolic groups in their molecular structure. Polyphenols are known to be 25 times more effective than Vitamin E and 100 times more effective than Vitamin C in neutralizing free radicals [4].

Polyphenols are widely distributed in various plants [5], including cocoa husks. Indonesia is the third-largest cocoa exporter globally, producing approximately 720.66 thousand tons of cocoa beans in 2020 [6]. However, cocoa husks are often underutilized as waste, despite their significant potential for polyphenol extraction.

Traditionally, polyphenol extraction from cocoa husks is performed using the maceration method, which is time-consuming and energy-intensive [5]. To improve process efficiency, advanced extraction techniques such as ultrasonic-assisted extraction (UAE) have been developed. UAE utilizes ultrasonic waves to generate cavitation— the formation of microbubbles or cavities in a liquid medium during ultrasonic wave cycles [7]. These cavitation bubbles collapse under high pressure, causing surface peeling, erosion, and particle disintegration [5,8]. This mechanism enhances the extraction process by reducing diffusion barriers and shortening extraction time.

Furthermore, the type of solvent used in the extraction process significantly affects the yield. Solvent selection is based on factors such as selectivity, toxicity, ease of evaporation, and cost [9]. Since polyphenols are polar compounds, polar solvents like distilled water, methanol, and ethanol are commonly used [10]. However, Niemczewski (1980) found that cavitation intensity in water is higher compared to organic solvents such as methanol and ethanol [11]. This difference is due to the varying ultrasonic wave propagation speeds in different media [12], which influence cavitation bubble formation and, consequently, the extraction yield.

In addition to solvent selection, material drying is a common pre-treatment in extraction processes. According to Cante (2021), drying enhances extraction efficiency because moisture can hinder solvent penetration into plant matrices. Thus, samples with lower moisture content typically yield higher extraction rates [13]. However, considering that polyphenols are polar and can be effectively extracted with water [14], extraction without prior drying is feasible. Moreover, drying consumes substantial energy, increasing operational costs, especially given that fresh cocoa husks contain up to 80% moisture [15].

Therefore, this study aims to investigate the effects of material drying and solvent type on the polyphenol extraction process from cocoa husks using ultrasonic-assisted extraction, with a focus on evaluating the economic implications.

2. Research and Methodology

2.1 Materials (Heading two)

The materials used in this study include cocoa husks obtained from local farmers in the Lampung region, distilled water, 96% ethanol, and 95% methanol. The equipment setup used in this research is shown in Figure 1, consisting of an ultrasonic bath, 120-mesh sieve, analytical balance, stirring rod, filter paper, funnel, 150 mL and 250 mL beakers, volumetric pipette, hot plate, centrifuge, and a kWh meter. The study was conducted using the ultrasonic-assisted extraction (UAE) method. The experimental variables include different solvent types—96% ethanol, 95% methanol, and distilled water—and material drying treatments, comparing dried materials with a moisture content of approximately 11% to undried materials. The extraction process was performed using 15 g of cocoa husk with 150 mL of solvent as constant variables. Extraction times ranged in 20-minute intervals up to 100 minutes using a 40 kHz ultrasonic bath.

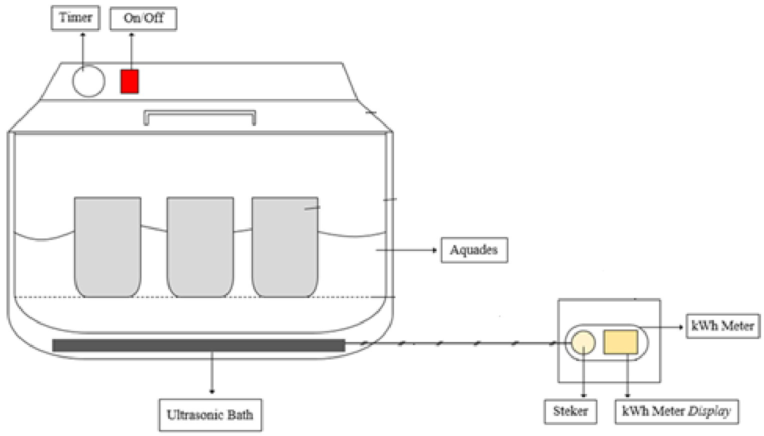


Figure 1. The ultrasonic bath apparatus consists of a beaker containing the sample, covered with aluminum foil, and connected to a kWh meter

2.2 Experiments

The cocoa husks were prepared according to the treatment variations. A portion of the material was dried in an oven at 60°C until it reached a moisture content of approximately 11%, while the rest remained undried. The dried cocoa husks were then ground and sieved through a 120-mesh sieve. For each experiment, 15 g of cocoa husk powder was placed in a 150 mL beaker, followed by the addition of 150 mL of solvent based on the solvent variation. The beaker containing the material and solvent was then placed in the ultrasonic bath, and the extraction process was initiated. At each extraction interval, the beaker was removed, and the time was recorded. This process was repeated for the remaining extraction times. During the extraction, the power consumption of the ultrasonic bath was measured using a kWh meter connected to the power outlet

After extraction, the mixture of solvent and extracted material was filtered using filter paper. A 5 mL aliquot of the filtrate was collected with a volumetric pipette and analyzed using UV-Vis spectrophotometry to determine the phenolic content. Additionally, conventional extraction was performed using the maceration method as a control, with 96% ethanol as the solvent at room temperature. The maceration time used was based on the optimum extraction time identified in the UAE process with ethanol. Subsequent analysis was conducted using UV-Vis spectrophotometry. Gallic acid solution was used as a standard solution to calculate the total phenolic content [16].

2.3 Product characterization

The products (biomass biochar and hybrid biochar) recovered from the process were characterized to ascertain some of their properties using Scanning Electron Microscope with energy Dispersive X-ray Spectroscopy (SEM-EDS), Fourier Transform Infra-Red Spectroscopy (FTIR) and Brunauer-Emmet-Teller (BET) analysis. Scanning Electron Microscopy (SEM, Phenom proX, Phenom-World BV, Netherlands) was used to study the surface morphology of the particles of the biochar. A double adhesive was placed on a sample stub. The sample was sprinkled on the sample stub and subsequently taken to a sputter coater (quorum-Q150R Plus E) and coated with 5 nm of gold.

3. Results and Discussion

The results of polyphenol extraction based on the type of solvent are shown in Figure 2. It can be seen that there are differences in phenolic yields during the extraction process. In samples using distilled water as the solvent, the phenolic content of the extracts was 161.7522, 162.4920, 220.1248, 186.0200, and 178.2037 mg GAE/g. In samples using methanol as the solvent, the phenolic content of the extracts was 70.6748, 81.7607, 79.7859, 76.5774, and 69.0142 mg GAE/g. Meanwhile, in samples using ethanol as the solvent, the phenolic content of the extracts was 57.7984, 54.5916, 60.5612, 58.4643, and 68.3596 mg gae/g. Each treatment was conducted with extraction times of 20, 40, 60, 80, and 100 minutes.

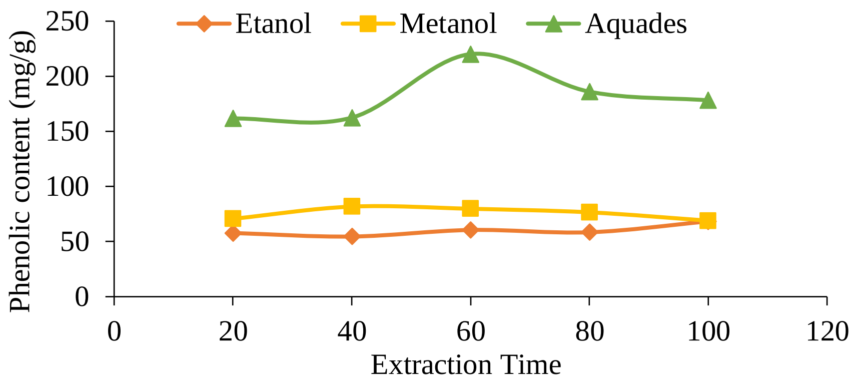


Figure 2. Extraction Results for each Solvent Type

Based on these results, the highest phenolic content was obtained when using distilled water as the solvent, while the lowest phenolic content was obtained when using ethanol. However, the highest yield was achieved when using ethanol. As a result, the total polyphenols extracted, based on both phenolic content and yield, showed that ethanol extraction yielded more than methanol extraction. In terms of both phenolic content and total phenolics, cocoa pod husk extraction using distilled water as the solvent resulted in the highest yield. This is due to the ultrasonic waves causing cavitation effects that can disrupt or damage the cell walls, making it easier for the compounds inside to be released [17].

Cavitation activity can create microjets that damage cell walls, reduce particle size, and increase surface area, thus enhancing the mass transfer rate [18]. According to Niemczewski (1980), distilled water has a maximum cavitation value of 100% [11]. Therefore, the diffusion process of target compounds proceeds faster when using distilled water compared to ethanol and methanol, making distilled water the most effective solvent for extraction.

Polyphenols are compounds that dissolve in polar solvents, thus solvents such as distilled water, methanol, and ethanol can be used [10]. From the use of distilled water in Figure 1, it is evident that an extraction time of 60 minutes resulted in the highest yield, while the lowest yield was obtained at 20 minutes. Cocoa pod husks are known to contain pectin ranging from 8 to 11.31% [19]. Pectin is a water-soluble polysaccharide derivative containing methoxyl groups [20]. These methoxyl groups influence gel formation properties, where gels can form through hydrophobic cohesion and hydrogen bonding [19].

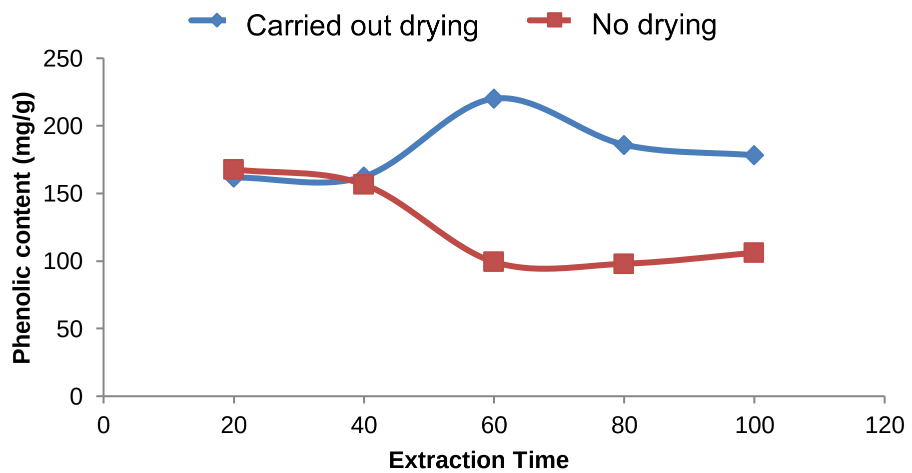
Hence, in the experiment, the samples extracted with distilled water showed a slightly thick consistency, and after the extraction process, the extract mixture became thicker over time. From 20 to 60 minutes of extraction, there was an increase in phenolic yield. This aligns with the principle of extraction, where longer extraction times generally result in higher yields. However, at 80 and 100 minutes, no further increase was observed. This may be due to increased gel formation from pectin, making it difficult for target compounds to diffuse. The presence of this gel also complicates the separation of dissolved substances from solids, resulting in lower extract weights when using distilled water compared to ethanol and methanol.

The total phenolic yield using ethanol was higher than that using methanol. When considering maximum cavitation values, the percentages for ethanol and methanol are not significantly different. Methanol has a slightly higher value than ethanol, with methanol at 52% and ethanol at 46%. On the other hand, polarity levels influence the extraction of cocoa pod husks. Methanol has a higher polarity with a dielectric constant of 33.60, while ethanol's is 24.30 [21]. The phenolic compounds in cocoa pod husks have polarity levels closer to that of ethanol, allowing more phenolic compounds to dissolve in ethanol. This is consistent with research conducted by Anggreni (2019), where phenolic yields were higher with ethanol [22].

Therefore, in cocoa pod husk extraction using ultrasonic waves, solvent polarity is believed to have a greater influence when maximum cavitation values are similar. Consequently, phenolic yields are higher with ethanol than with methanol. However, regarding the yield, ethanol's polarity dissolves more other polar compounds from cocoa pod husks, resulting in a lower phenolic content percentage in the extract compared to methanol.

Based on the research results, the lowest sample and operational conditions were found in samples extracted with methanol for 20 minutes, yielding 70.6748 mg gae/g phenolic content, 102.1251 mg total phenolics, with a 9.63% yield and 7.07% phenols. In contrast, the most optimal sample and operational conditions for phenolic extraction from cocoa pod husks were achieved using distilled water for 60 minutes, yielding 220.1248 mg GAE/g phenolic content, 262.3887 mg total phenolics, with a 7.95% yield and 22.01% phenols.

The polyphenol extraction results based on material drying treatments are shown in Figure 3, with distilled water as the solvent for this treatment. It is evident that there are differences in phenolic yields during the extraction process. In samples that were dried using an oven before extraction, the phenolic content of the extracts was 161.7522, 162.4920, 220.1248, 186.0200, and 178.2037 mg GAE/g, with extraction times of 20, 40, 60, 80, and 100 minutes, respectively. Meanwhile, in samples that were not dried, the phenolic content of the extracts was 162.0054, 159.5632, 99.3016, 97.9966, and 106.0603 mg GAE/g at extraction times of 20, 40, 60, 80, and 100 minutes, respectively.



Figur 3. Hasil Perlakuan Pengeringan Bahan

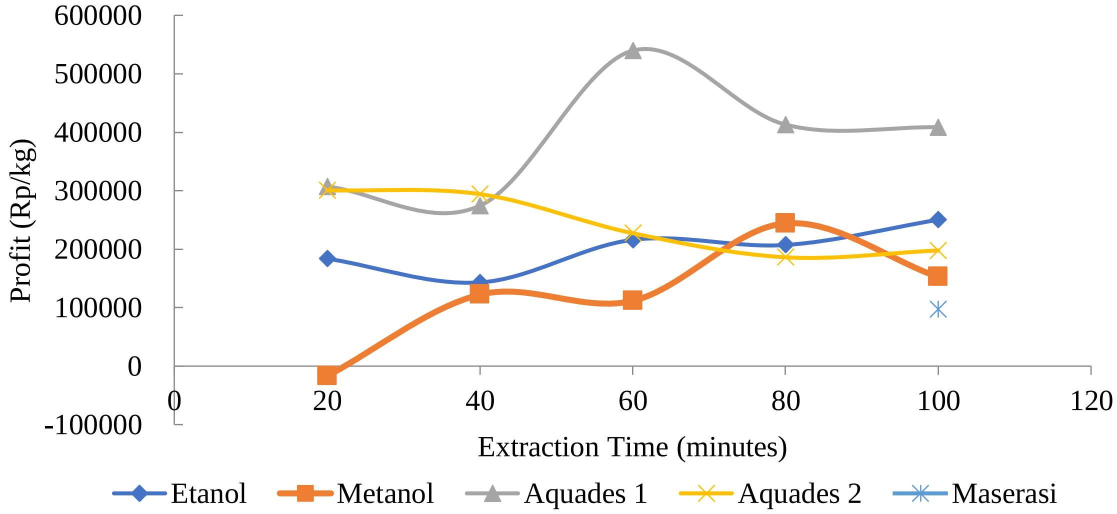
Based on these results, the samples with material drying before extraction showed higher phenolic content, while the samples without drying showed lower phenolic content. This indicates that drying before extraction can increase the phenolic yield in the extract. According to Cante (2021), drying can improve the efficiency of the extraction process, as indicated by the higher concentration of oil obtained along with the lipid fractions extracted with water in the samples [13].

The increase in phenolic yield is suspected to occur because, during the drying process, cell wall degradation in the sample takes place. It has been explained that thermal processes can disrupt cell walls. Target compounds are dissolved in complex cells, and the cell wall becomes the main barrier that affects the permeability of solutes. The natural plant structure, especially the cytoplasmic membrane and cell walls, limits the fluid transfer process. Mechanical, thermal, chemical, or biological methods can be proposed to disrupt cell walls. The thermal process in drying can be used to disrupt cell walls. Heat-induced denaturation can reduce resistance to solute diffusion across cells through the cell walls and membranes, increasing permeability but lowering selectivity [5]. Therefore, extraction is more optimal in samples that have been dried.

From Figure 3, it can be seen that the dried samples experienced an increase in phenolic yield as the extraction time increased, up to 60 minutes of extraction. However, the yield then decreased at 80 and 100 minutes. This is suspected to occur because cocoa pod husk samples contain pectin, which leads to greater slime formation during extraction at 80 and 100 minutes. In contrast, the wet material initially extracted more phenolics, but the yield decreased over time. This is because, at first, phenolics were still able to diffuse, but over time, pectin reacting with water formed slime more rapidly.

Therefore, from the research results, it is found that the lowest sample and operational conditions were for the samples without drying, and the extraction time of 80 minutes, where the phenolic content obtained was 97.9966 mg gae/g with a yield of 8.43% and 9.8% phenolics. In contrast, the most optimal sample and operational conditions for phenolic extraction from cocoa pod husks were for the dried samples with an extraction time of 60 minutes, where the phenolic content obtained was 220.1248 mg GAE/g with a yield of 7.95% and 22.01% phenolics.

Polyphenols are antioxidant compounds that can be used to prevent and inhibit the development of diseases caused by oxidative stress [23]. Therefore, polyphenols have a relatively high market value. The process of obtaining polyphenols from cocoa pod husks is extracted and goes through a series of processes that require costs, including solvents, electricity, and others. The resulting extract can then be sold to consumers and priced based on the percentage of polyphenols obtained [24][25]. After determining the selling price and cost price, the profit from the process is obtained by reducing or subtracting the difference in those prices.



Figur 4. Profit Extraction Process

From Figure 4, it can be seen from an economic standpoint that aquades 1 represents the sample that underwent material drying treatment, while aquades 2 represents the sample without material drying treatment. The most optimal operational and sample conditions were the sample with aquades solvent and material drying treatment, with an extraction time of 60 minutes, where the profit obtained per 1 kg of extract was Rp. 539,683.05. In contrast, the lowest sample and operational conditions were the sample with methanol solvent and material drying treatment with an extraction time of 20 minutes, where the loss per 1 kg of extract was -Rp17,075.41. This is due to the low yield and phenolic percentage produced under these conditions. Therefore, the extraction of polyphenols from cocoa pod husks using the ultrasonic assisted extraction method has great economic potential. This is supported by the greater extract yield and profit when using the ultrasonic assisted extraction method compared to the maceration method.

4. Conclusion

Based on the research results, it is known that the best condition for the ultrasonic assisted extraction method of polyphenols from cocoa pod husks is using aquades as the solvent with material drying treatment. The best extraction result occurs at an operating time of 60 minutes, yielding 7.95%, with a phenolic content of 22.01% or 220.1248 mg gae/g. This process also has great economic potential, as the ultrasonic assisted extraction method for polyphenol extraction from cocoa pod husks provides significant profit, with the highest profit obtained being Rp539,683.05/kg for the 60-minute aquades extraction. The polyphenol extraction process from cocoa pod husks using the ultrasonic assisted extraction method is considered economically feasible because the extract yield and economic profit obtained are greater than those from the maceration method.

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Conflict of Interest: The authors declare that there are no conflicts of interest.

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