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Pectin Extraction from Cocoa Pod Husk Prepared with Various Drying Temperature and Extracting Solvents

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Cocoa pod husk is an agricultural waste from cocoa bean processing. It is an excellent source of pectin, which has great advantages as dietary fiber, thickening agent, and food texture stabilizer. This study aims to investigate the efficiency of pectin extraction from cocoa pod husk dried at different temperature (sun-drying, 50°C and 85°C) as well as the use of various extracting solvents (citric acid vs acetic acid solution, concentrations at concentrations 5, 12.5, and 25% v/v, pro analysis vs technical grade). The extraction was carried out at 95°C for 5 hours. The results showed that the drying temperature of cocoa pod husk, besides the types and concentrations of solvent have induced differences in yield and characteristics of the crude pectin. The drying of cocoa pod husk at 50°C was associated with higher yield and water holding capacity of the pectin. In addition, higher pectin yield was also obtained from the extraction using aqueous citric acid solution (5%, pro analysis). However, there were possibilities for substitution with different acid and technical grade solvent. This finding could be used as a basis for pectin production from cocoa pod husk at industrial level.

Keywords: Pectin; cocoa pod husk; yield; acid; solvent

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Pectin is a soluble fiber with numbers of health benefits [1], and an important additive in food manufacturing [2]. It is contained in fruits, of which apple and citrus peels are the main sources [3]. Cocoa pod husk (CPH) is a potential alternative source for pectin, whereas its pectin content ranging from 6-9% [4]. The weight of cocoa pod husk accounts for 75% of the total weight of cocoa pod [5]. It is currently considered as an agricultural by-product, that is mainly processed for compost making [5].

The extraction of pectin from CPH has been reported [4, 6, 7]. However, in a large-scale production, the quality of CPH as raw material is one of important factors influencing the pectin yield. The CPH may be supplied in dried forms in order to reduce transportation load and extend the storage time [5]. The drying of CPH could be carried out at various different temperature, including sun-drying and mechanical drying at 50°C and above 60°C [8]. Another factor is the acidic solution as a mean of extraction. Previous studies have demonstrated the use of citric acid, acetic acid, and some other acids [4, 9]. The difference in the type of acid affects the homogalacturonan content, integrity and length of polymer [10]. Moreover, the quality of the acid was also influenced by the purity of the solutions [11], thus the use of different acid grade (pro analysis and technical grade) should be taken into consideration.

In this study, the effects of drying temperature of the CPH were investigated with respect to the extraction yield and the properties of the pectin. Correlational analysis was conducted to assess the relationships between the parameters of CPH (drying temperature, drying time, moisture content, total polyphenol content, and browning index) and the pectin (yield, water holding capacity and solubility). Furthermore, the influences of different acid solutions (citric acid and acetic acid), concentrations and grades (pro analysis and technical) on the pectin yield was also evaluated.

EXPERIMENTAL

Chemicals and Materials

Cocoa pod husk (CPH) from mixed varieties was obtained from Indonesian Coffee and Cocoa Research Institute, East Java, Indonesia. The CPH was cut to size 4-5 cm and processed with sun-drying, oven drying at 50°C and 85°C. The drying was terminated when the CPH weigh was no longer decreasing. The dried CPH was then ground and stored in polyethylene bags at room temperature until use. The chemicals comprised of technical grade ethanol (97% purity), citric acid (pro-analysis, Sigma), acetic acid (pro-analysis, Sigma). In addition, technical grade citric acid (Gajah brand) and acetic acid (Kura-kura brand) were bought from local food supply stores.

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Pectin Extraction

The pectin extraction from CPH was performed according to [4] with 5 hours incubation at 95°C.

Characterization Methods

The characterization of CPH comprised of moisture content [12], total polyphenol content [13], and browning index [14]. The extraction yield of pectin was determined from the percentage of the pectin dry weight from the CPH dry weight. The characterization of pectin was consisted of water holding capacity and solubility [15].

Statistical Analysis

The mean and standard deviation values were determined from three replications. The data were tested for normality of distribution (Shapiro-Wilk's test) and homogeneity of variances (Levene's test) prior to Analysis of Variances and Tukey post-hoc tests. In case the normal distribution was not achieved, the data were data proceeded into Kruskal-Wallis non-parametric test. The statistical analyses were performed using SPSS software (version 17, IBM) at 95% confidence level.

RESULTS AND DISCUSSION

The drying of the cocoa pod husk at different temperatures has resulted variations in the duration of drying and the moisture content of the dried cocoa pod husk. As expected, the longest drying time was observed in the sun-drying (14 days), while the time required for drying at 50°C and 85°C were 4 days. The moisture content of CPH chips after drying sun-drying was the highest at 13.8%, while after drying at 50°C and 85°C were 11.2% and 8.5% respectively (Figure 1).

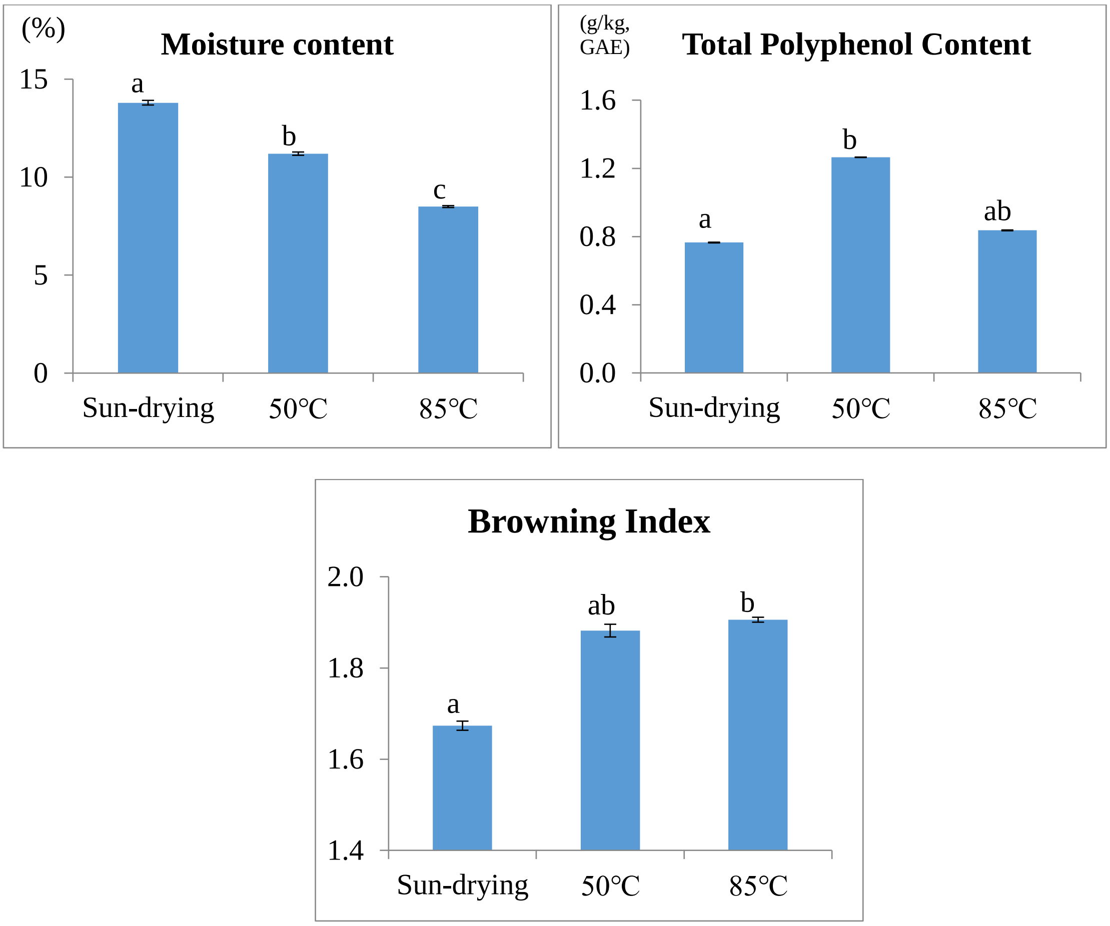

Figure 1. Characteristics of cocoa pod husk after drying at different temperatures. Bars were mean of three replications, lines were standard deviations. Bars with same letters were not significantly different according to Kruskal-Wallis test at 95% confidence interval.

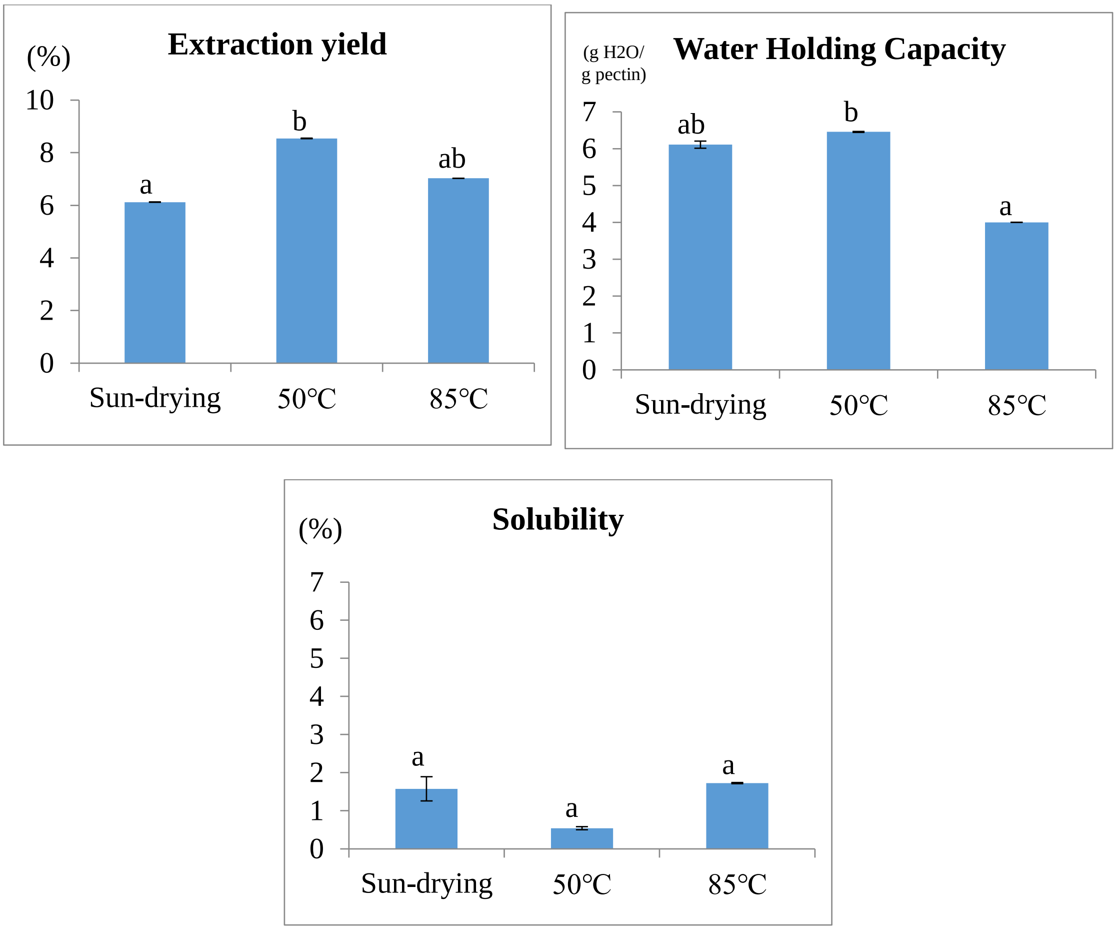

Figure 2. Extraction yield, water holding capacity, and solubility of pectin extracted from cocoa pod husk dried at different temperatures. Bars were mean of three replications, lines were standard deviations. Bars with same letters were not significantly different according to Kruskal-Wallis test at 95% confidence interval.

The appearance of the dried cocoa pod husk also varied after being dried at various drying temperature. Since the color is related with the polyphenolic compounds, the total polyphenol content and the browning index were determined. The CPH from sun-drying and drying at 85°C were characterized with lower total polyphenol content, than that from drying at 50°C. The browning index from sun-dried CPH was the lowest among other treatments (Figure 2).

The CPH dried at 50°C resulted pectin with the highest extraction yield and water holding capacity (WHC) than the other treatments. The solubility of pectin from this treatment did not significantly differ from other treatments.

Table 1. Pearson's correlational coefficients of the drying temperatures and the characteristics of dried cocoa pod husk with respect to the yield and properties of the extracted pectin. The asterisk symbol indicated the level of significance, $p < 0.05$ (*) and $p < 0.01$ (**).

	Temperature	Duration	Moisture	Polyphenol	Browning	Yield	WHC	Solubility
Temperature	1	$-.731^{*}$	$-.976^{**}$	-0.094	$.787^{*}$	0.058	$-.909^{**}$	-0.19
Duration	$-.731^{*}$	1	$.860^{**}$	-0.61	$-.992^{**}$	-723^{*}	0.383	-0.525
Moisture	$-.976^{**}$	$.860^{**}$	1	-0.121	$-.901^{**}$	-0.27	$.798^{**}$	-0.024
Polyphenol	-0.094	-0.61	-0.121	1	0.533	$.988^{**}$	0.497	$.986^{**}$
Browning	$.787^{*}$	$-.992^{**}$	$-.901^{**}$	0.533	1	0.654	-0.464	0.442
Yield	0.058	$-.723^{*}$	-0.27	$.988^{**}$	0.654	1	0.36	$.960^{**}$
WHC	$-.909^{**}$	0.383	$.798^{**}$	0.497	-0.464	0.36	1	0.579
Solubility	-0.19	-0.525	-0.024	$.986^{**}$	0.442	$.960^{**}$	0.579	1

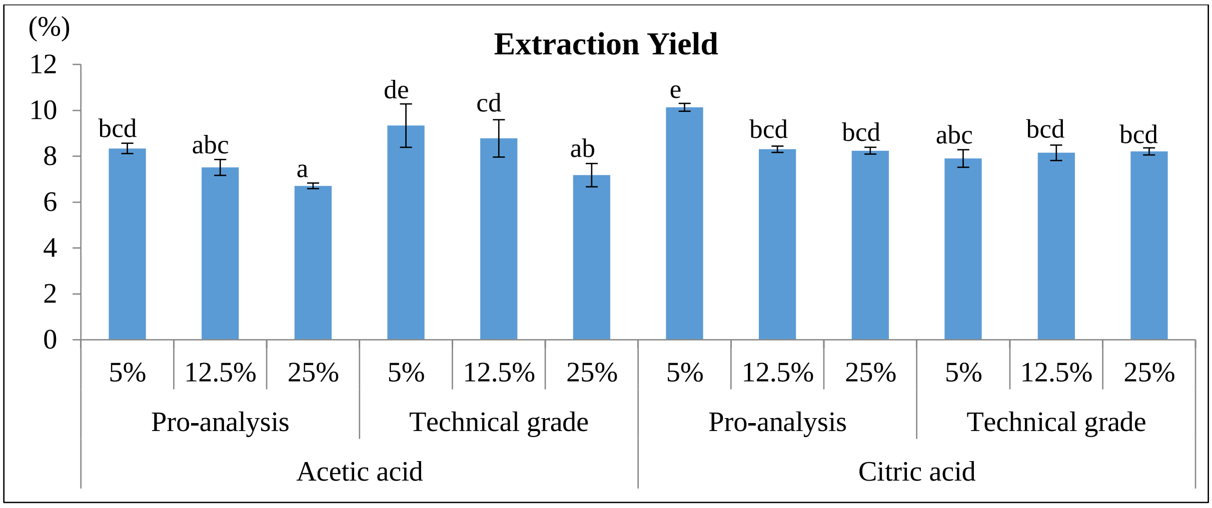

Figure 3. Extraction yields of pectin from cocoa pod husk extracted with different aqueous acid solutions. Bars with same letters were not significantly different according to Kruskal-Wallis test at 95% confidence interval.

Correlational analysis of the drying parameters and the characteristics of dried CPH towards the yield and properties of pectin was performed. It was demonstrated that the drying temperature was strongly correlated with the browning of CPH ($r = 0.757$, $p < 0.05$), but not with total polyphenol content ($r = -0.094$, $p > 0.05$). There were correlations between extraction yield and the duration of drying ($r = -0.723$, $p < 0.05$) as well as total polyphenol content ($r = 0.988$, $p < 0.01$). The water holding capacity of pectin was correlated with drying temperature ($r = -0.909$, $p < 0.01$) and moisture content ($r = 0.798$, $p < 0.01$) of CPH. The solubility of pectin was correlated with the total polyphenol content of CPH ($r = 0.986$, $p < 0.01$). In addition, higher extraction yield corresponded to the solubility of the pectin ($r = 0.960$, $p<0.01$).

The effects of different aqueous acid solutions on the extraction yield of pectin was also observed (Figure 3). The yield value varied from 6.7 to 10.1%, whereas the highest yield was found after extraction of CPH with citric acid solutions (5%, pro-analysis). The pectin yield was significantly influenced by the concentrations of the extracting solvents, but not by the type of acid (acetic vs citric acid) and solvent grades (pro-analysis vs technical grade).

The drying temperature represents the possible preparations at cocoa producer levels. Sun-drying was an economical method; however, it required longer time while producing CPH chips with high moisture content. Shorter drying time and lower moisture content in CPH were demonstrated from drying at the temperature of 50°C and 85°C, which could be carried out using mechanical dryer. The total polyphenol content of CPH from sun-drying and drying at 85°C were lower than that of treatment at 50°C. The polyphenols might have been oxidized by polyphenol oxidase, naturally available in the CPH. Lower temperature occurring in the sun-drying treatment might have allowed the polyphenol oxidase to retain its activity [16]. The product of polyphenol oxidation is the polymerized molecules with brown color, contributing to the enhanced value of browning index [17]. On the other hand, non-enzymatic browning has probably occurred in the CPH during drying at 85°C. Sugar, as one of the components of CPH, could be caramelized and forming brown color at high temperature [18].

During sun-drying, enzymatic activities might have also induced the decrease in the pectin extraction yield. The enzymes involved in the pectin degradation comprised of pectin methylesterase and pectin lyase [19]. Pectin methylesterase catalyzes the disconnection of the methyl branches from the polygalacturonan backbone, meanwhile pectin lyase catalyzes the splitting of the backbone [19]. The decrease in the branch and backbone length had probably enhanced the dissolution of pectin in the acidic solution which impede the recovery of pectin, hence decreasing the extraction yield [20, 21].

The treatment of CPH at 85°C had resulted pectin with lower water holding capacity. The water holding capacity was affected by the abundance of branch and the length of the polygalacturonan backbone [22]. The high temperature at 85°C had possibly decreased the enzyme activities, including pectin methyl esterase and pectin lyase in the CPH [23]. Thus, instead of enzymatic reactions, the decrease in water holding capacity might be attributed to hydrolysis that induces the splitting of glycosidic bonds between to galacturonan. It has been reported that polygalacturonan depolymerization could occur at temperature 60°C and humidity at 80% [24].

The CPH treatment at 50°C has resulted pectin at highest extraction yield with the greatest water holding capacity. The drying at this temperature had potentially inhibited the activity of the enzymes, thus obstructed the debranching and depolymerization of the pectin [23]. Additionally, the temperature was not too high so that sugar caramelization and hydrolysis could be avoided [25]. The drying at 50°C could be recommended to cocoa producers in preparing the CPH for mass production of pectin.

Finally, the use of various acidic solvents at different concentrations and grades has demonstrated the flexibility in pectin extraction method. Even though the highest pectin yield was obtained from citric acid extraction (5%, pro-analysis), there were no significant differences in the pectin yield arising solely from the type of acid. Therefore, acetic acid could be a substitution of citric acid. The use of acetic acid has been reported to increase the molecular weight, galacturonic acid content and degree of esterification of the extracted pectin [9]. Furthermore, since pectin yields were not significantly different between pro-analysis and technical grade solvents, the technical grade was considered sufficient for extraction.

The findings from this study provide important factors for the production of pectin at industrial setting. The raw material could be supplied from cocoa producers. The preparation of CPH chips could be standardized by requesting the producers to perform drying of CPH at 50°C. Subsequently, the production of pectin could be carried out by using citric acid or acetic acid at 5% concentration in water. Furthermore, economical production could be achieved by using technical grade solvents instead of the pro-analysis type.

CONCLUSION

It was concluded from this study that the drying temperature of CPH had affected the extraction yield and characteristics of pectin. The drying at 50°C was considered optimum, since it might have halted the enzymatic deterioriation while avoiding thermal degradation, resulting pectin at the highest extraction yield and water holding capacity. In addition, the yield of pectin extraction was influenced by the concentration of acidic solutions, but not by the type and the rade of the acids. This suggested the flexibility to use the acidic solutions. The findings provide recommendation for raw material standardization of raw material and as well as options for extracting components.

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