Optimization of NaOH concentration and cooking time in delignification of mature coconut (Cocos nucifera L.) coir

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Abstract. The main product of mature coconuts is coconut meat, while its by-products consisting of coconut water, shell fiber and coir. Coconut coir contains 75% fiber and 25% cork. The high value of fiber in coconut coir provides an opportunity to be utilized in making paper. Coconut fiber has a cellulose content of 26.6% - 43.44% and lignin of 29.4% - 45.84%. Due to the high lignin content, delignification process should be carried out which can be done using sodium hydroxide (NaOH). This study aims to obtain the optimal point of addition of NaOH and cooking time to produce optimal cellulose and lignin levels in the delignification of the mature coconut fiber pulping process. The research method uses the Response Surface Methodology (RSM) with two factors and two optimized responses. The experimental design was performed with a central composite design. The variables involved were NaOH concentration (5-15%) and cooking time (90-150 minutes). Two responses studied were lignin and cellulose content. The combination of these treatments produces the optimum point of NaOH concentration of 5% and cooking time of 150 minutes, resulting in 15.56% lignin content and 37.29% cellulose content.

1. Introduction
Papemaking uses wood as raw materials, which detrimental to the environment. The supply of natural forest timber is struggling to match the growth of the pulp and paper industry [1]. This finding was worsened by pulp exports in 2010 reaching 2.6 million tons [2]. In addition to the increasing capacity of the pulp and paper industry, the demand for handmade paper in Indonesia has been significantly increased, but the supply of pulp for handmade paper is still far from the expected figure, which about 4 million tons per year [3]. The high demand for pulp and the low wood raw material for pulp production, particularly in Indonesia requires innovation in the manufacture of pulp with raw material from waste, for example, coconut waste.

The coconut tree (Cocos nucifera L.) serves as a plant that fulfills economic, social, and cultural needs, and is associated as the tree of life due to all usable parts [4]. One of the most widely used parts of a coconut tree is the fruit. Coconut can be processed into nata de coco, coconut milk, and consumed directly in the form of coconut water and fruit flesh. However, those utilization means of the coconut leave the husk as its waste. Coconut husk is the outer portion of a coconut that encloses a coconut shell
with thickness ranging from 5-6 cm, consisting of exocarpium as the outer layer and endocarpium as the inner layer. One coconut fruit contains 30% of the husk, which approximately 0.4 kg whole coconut [5]. The husk consists of cellulose, lignin, pyroligneous acid, gas, charcoal, tar, tannin, and potassium [6]. Coir or coconut fibre, is a natural fibre extracted from the outer husk of coconut.

Untreated coconut coir waste is generally burned, causing breathing issues for the surrounding community. Coconut coir is commonly utilized as a product with more economic value to reduce the burning process of coconut coir waste. Fine coir can be utilized as a material for ropes, sacks, pulp, carpets, brushes, doormats, heat and sound insulation, filters, seat/car seat fillers, and hardboard boards. The high production of coir provides an opportunity to be utilized for handmade paper industry material.

Handmade paper is a type of paper with a unique texture and appearance derived from used paper to agricultural waste pulp [7]. The utilization of handmade paper is mostly for handicrafts, such as tissue boxes, invitation cards, greeting cards, and other products. The main component of making pulp is cellulose. Papermaking from raw materials other than wood has been of interest, and one of them is from coconut coir. Coconut coir contains 75% fibre and 25% cork [6]. The coir consists of cellulose content (26.6%-27.7%) and lignin content (29.4%) [5]. The high cellulose content in coconut coir can improve the quality of handmade paper, despite high content of lignin content in its coir. Lignin has been utilized for fillers [8]. However, the presence of lignin in the paper is resulting in a stiff and brownish paper [9]. Lignin in the coir inhibits the bond between fibres; thus, it is necessary to remove the lignin, known as delignification.

The delignification is a process of dissolving lignin in a solvent, aiming to break lignin bonds during the process of pulp cooking to obtain more fibre. In the present research, the response surface method, a common method for optimization [10] was used for optimizing the cellulose content and reducing the lignin content. The results of this study can be utilized as a reference for the treatment of coconut coir delignification process and alternative wood substitutes in papermaking, specifically handmade paper.

2. Materials and Methods

2.1 Material

The materials used in the delignification process were coconut coir (obtained from Kebonagung, Pakisaji, Malang, East Java) derived from 13 weeks old coconut, sodium hydroxide (NaOH) p.t. (pro technics) of 78%, aluminum foil, and aquades (H₂O). Besides, materials used to test the contents of lignin and cellulose include sulfuric acid (H₂SO₄) p.a (pro analyst) 98%, aquades, and clay. The equipment used in the delignification process included digital scales, beaker glass, blenders, ovens, filter cloths, hot plates, stopwatches, scissors, stirrers, and measuring cups; while the tools used to test the contents of lignin and cellulose are reflux, petri dishes, ovens, hot plates, scales, Erlenmeyer, desiccators, porcelain cups, tongs, muffle furnaces and gloves.

2.2 Delignification process

In the delignification process, the coconut coir was washed with flowing water and heated in distilled water to remove impurities. The coir was then aerated in the sun for five days. Dry coconut coir was then cut with a length of 2 cm to help speeding up the delignification process. The delignification process was carried out by submerging the coir in a heated NaOH solution at a temperature of 100°C for 90 - 150 minutes (according to the treatment). After delignification process, the cellulose and lignin content were tested using Chesson Methods.

2.3 Methods

The optimization of delignification process was done by using Response Surface Method with a Central Composite Design. The treatment factors include NaOH concentration and cooking time. The experiment was conducted by using the midpoint (X = 0) with the first factor (NaOH) midpoint concentration of 10% (X₁ = 0) and the second factor (cooking time) midpoint for 120 minutes (X₂ = 0). Determination of the midpoint of the factor was based on literature which indicated that the highest
The cellulose content in coconut coir was obtained by using a 10% NaOH cooked for 120 minutes, resulting in a cellulose content of 88.50% [11]. The lowest lignin content obtained by using the 10% NaOH treatment cooked for 90 minutes was equal to 3.28%.

The data obtained were then analyzed by using Design Expert 10.0 1 to determine the limits of the delignification process [12]. The factors include NaOH concentration factor and cooking time factor with 3 contents of -1, 0, and 1. The centralized composite design is as shown in Table 1.

Table 1. The centralized composite design.

| No | X1  | X2  | NaOH Concentration (%) | Cooking Time (minute) | Cellulose Content (%) | Lignin Content (%) |
|----|-----|-----|-------------------------|-----------------------|-----------------------|-------------------|
| 1  | -1  | -1  | 5                       | 90                    | 23.37                 | 23.63             |
| 2  | 1   | -1  | 15                      | 90                    | 35.42                 | 15.71             |
| 3  | -1  | 1   | 5                       | 150                   | 37.33                 | 17.32             |
| 4  | 1   | 1   | 15                      | 150                   | 25.38                 | 20.81             |
| 5  | -1.414 | 0  | 2.92893                 | 120                   | 26.79                 | 19.08             |
| 6  | 1.414 | 0  | 17.0711                 | 120                   | 27.26                 | 19                |
| 7  | 0   | -1.414 | 10                       | 77.57                 | 22.52                 | 22.86             |
| 8  | 0   | 1.414 | 10                       | 162.42                | 33.94                 | 16.01             |
| 9  | 0   | 0   | 10                       | 120                   | 35.07                 | 15.9              |
| 10 | 0   | 0   | 10                       | 120                   | 31.67                 | 15.81             |
| 11 | 0   | 0   | 10                       | 120                   | 32.17                 | 15                |
| 12 | 0   | 0   | 10                       | 120                   | 33.83                 | 15.74             |
| 13 | 0   | 0   | 10                       | 120                   | 32.94                 | 15.71             |

3. Results and Discussion

3.1 Coconut coir

Table 2 shows the lignin and cellulose content before the delignification process. The results of the material testing obtained value of lignin content which was quite high due to mature coconut coir originating from the dark coconut waste which had a dark brown color. The high content of cellulose in coconut coir has the potential to be used as handmade paper pulp, but a delignification process is required to reduce the lignin content. The optimization process is required to obtain the optimal point with a minimum value of lignin content and a maximum value of cellulose content.

Table 2. Coconut coir content.

| Coconut coir   | Value (%) |
|----------------|-----------|
| Lignin content | 61.42     |
| Cellulose content | 22.58   |

3.2 The cellulose contents

Table 4 shows the cellulose content. The highest cellulose content was obtained in the treatment of 5% NaOH concentration with a cooking time of 150 minutes, producing cellulose contents of 37.33%. Analysis of cellulose content in the table fit summary suggested quadratic mathematical models of 2FI, with the value of Adjusted R Squared of 0.7564. This result indicated that the model closed to the
response. In the analysis of variance (ANOVA), the mathematical model for the response of cellulose content was a quadratic model with a p-value of 0.0070. The p-value is less than 0.05, indicating that the mathematical model has a significant effect on response. There was a lack of fit value, which was a p-value of 0.0562, indicating an insignificant value because the p-value is more than 0.05 presenting errors that do not affect the model.

Based on the analysis of variance in the ANOVA, it was apparent that NaOH did not significantly influence the cellulose contents (p-value > 0.05 = 0.9130). Meanwhile, cooking time significantly influenced the cellulose contents (p-value < 0.05 = 0.0221). ANOVA results showed that the concentration of NaOH given did not affect the pulp cellulose content. This can be caused by environmental factors that influence the temperature of the delignification process and stirring during the delignification process. The stirring process affects the pulp making, the faster the stirring the higher the cellulose content of the pulp [13]. The polynomial equation in the form of an actual variable is as follows:

\[
Y = -62,83068 + 6,71226 X_1 + 0,95486 X_2 - 0,039986 X_1 X_2 - 0,094726 X_1^2 - 0,00196378 X_2^2
\]

The Y value is the cellulose content, with influencing factors namely X1 (NaOH concentration) and X2 (cooking time). Every time there is an addition of 1 point to X1 the value of cellulose content will increase by 6.71226 and likewise for the addition of 1 point to X2 will increase the value of cellulose levels because the factor coefficient has a (+) sign.

**Figure 1.** Relation between cooking time and NaOH concentration on the cellulose contents.

Figure 1 shows that higher NaOH concentration causes higher cellulose content. Whereas, longer cooking time factor results in higher hepatic cellulose contents. The result demonstrates the increasing fluctuation value, which is consistent with research conducted by [14] pointing out that the delignification process with 7.5% NaOH increases the grain cellulose content to reach 82.96%, and 15% NaOH increases the cellulose content by 98%. Cellulose degradation in the cooking process is also influenced by cooking temperature, in which greater change in temperature affects greater heat generated. The application of higher cooking temperatures will convert the degraded lignin to greater contents of cellulose in the pulp [15].
3.3. Lignin content

Table 4 shows the lignin contents of the samples. The highest lignin content in the treatment of 5% NaOH concentration with a cooking time of 90 minutes, producing lignin contents of 23.63%. The lowest lignin content (15%) was obtained at a concentration of 10% NaOH with a cooking time of 120 minutes. The lower value of lignin content results in a better quality of coconut coir pulp, which is following the optimization goal for minimizing the lignin content. Analysis of lignin contents in the table fit summary suggests a quadratic mathematical model, producing an Adjusted R Squared value of 0.8033, indicating that the model was close to the response. In the analysis of variance (ANOVA), the mathematical model for the lignin contents was a quadratic model with a p-value of 0.0034 (< 0.05), indicating that the mathematical model has a significant effect on the response. The model is supported by a lack of fit value (p-value of 0.0036).

Based on the analysis of variance in the ANOVA, it is apparent that NaOH concentration did not significantly influence lignin contents (p-value>0.05=0.2571), due to less high concentration. Meanwhile, cooking time has a significant effect on lignin contents (p-value < 0.05 = 0.0211). NaOH concentration did not significantly influence lignin contents, indicate that errors do not affect the mathematical model. The concentration of NaOH is too low for the delignification process with the value of the lignin content in the material, so the delignification process is not optimal, this is following the study [16], with the lignin content of the NaOH concentration used by 20% -30%. A mathematical model with two equations of polynomial equations including code variable and actual variable. The polynomial equation in the form of the actual variable is as follows:

\[
Y = +82.92647 - 3.78478 \times X_1 - 0.75131 \times X_2 + 0.019017 \times X_1 \times X_2 + 0.069460 \times X_1^2 + 0.00214889 \times X_2^2 \tag{2}
\]

The Y value is the lignin level, with the influencing factors, namely X1 (NaOH concentration) and X2 (cooking time). Every time there is an addition of 1 point to X1 the value of lignin levels will decrease and likewise for the addition of 1 point to X2 will reduce the value of cellulose levels because the factor coefficient has a sign (-).

**Figure 2.** The relations between cooking time and NaOH concentration on the lignin contents.

Figure 2 shows that higher NaOH addition resulted in lower lignin content. Whereas, longer cooking time results in lower lignin content. The finding also clarifies that higher NaOH concentration on lignin contents will decrease lignin contents. The OH⁻ ion in NaOH will break the basic bond in lignin and will
dissolve in the phenolic salt, formed by the Na\(^+\) bond with the lignin compound. Lignin is dissolved in a black NaOH solution, called a black leachate compound, in which higher NaOH concentration results in greater hydrolyzed lignin [17]. The greater temperature change will cause greater heat, degrading the lignin content as the cooking temperature will break down lignin contents into monomers [18].

3.4. Optimization of cellulose contents and lignin contents
The purpose of the study was to minimize lignin content and maximize cellulose content. The results indicated that lignin contents ranged from 15% to 23.63% and cellulose contents ranged from 22.52% to 37.33%.

### Table 3. Constraint limit for optimal solution results.

| Name          | Goal    | Lower Limit | Upper Limit | Importance |
|---------------|---------|-------------|-------------|------------|
| A: NaOH Concentration | In range | 5           | 15          | 3 (important) |
| B: cooking time   | In range | 90          | 150         | 3 (important) |
| Lignin content   | Minimize | 15          | 23.63       | 3 (important) |
| Cellulose content | Maximize | 22.52       | 37.33       | 3 (important) |

### Table 4. Optimal solution results.

| Item                  | Result  |
|-----------------------|---------|
| NaOH concentration    | 5%      |
| Cooking time          | 150 minutes |
| Lignin content        | 15.56%  |
| Cellulose content     | 37.29%  |
| Desirability          | 0.966   |

The optimum value of the delignification process of the coconut coir was found at 5% NaOH concentration with a cooking time of 150 minutes. Based on the optimization value, lignin content was 15.56% and cellulose content was 37.29%. The constraint limit of the optimal results towards the response is depicted in Table 4, indicating a desirability value of 0.966. There were excluding factors in the model that affect the optimization results, such as the temperature in the material drying process, which was not similar to the natural conditions that affect the material mass and the ratio of cooking solution. The high value of lignin and cellulose content produced under optimum conditions indicates that coconut coir has the potential to be used as a material for pulp in handmade paper making.

4. Conclusions
The delignification process was found optimum at the addition of 5% NaOH and cooking time of 150 minutes. This condition produces 15.56% lignin and 37.29% cellulose content in the coir. The high value of lignin and cellulose content produced at optimum conditions indicates that coconut coir has the potential to be utilized as a material for pulp in handmade paper making.

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