Ultrasound-assisted production of corn starch: Process design and optimization

R N Fathimah, A F A Ishlahi, M N Cahyanto, and W Setyaningsih*

Department of Food and Agricultural Product Technology, Faculty of Agricultural Technology, Gadjah Mada University, Yogyakarta, Indonesia

*Correspondance e-mail: widiastuti.setyaningsih@ugm.ac.id

Abstract. Most starch industries utilize maceration as the extraction method to recover starch from corn matrices; however, the production is time-consuming and often inefficient. Ultrasound-assisted extraction (UAE) appears to propose an enhancement of the extraction process. Hence, in this study, UAE has been developed to reach an optimum recovery in a short extraction time for starch obtaining from corn grain. Several extraction variables were studied, including ultrasound power ($x_1$, 30-90%), cycle ($x_2$, 0.3-0.9 s$^{-1}$), and solvent to sample ratio ($x_3$, 10:1-30:1 g ml$^{-1}$). A Box-Behnken design, coupled with Response Surface Methodology, was performed to optimize the three studied variables. The acquired mathematical model was used to estimate a predictive equation for the extraction yield. The model was validated based on an acceptable coefficient of determination ($R^2$, 0.88), a low mean absolute error, and the value of lack-of-fit suggested that the model was adequate in explaining the observed data at the 95.0% confidence level. The predicted optimum yield was achieved by applying UAE conditions as follows: 87% ultrasound power, 1.0 s$^{-1}$ cavitation cycle, and 30:1 solvent to sample ratio. Additionally, a two-cycle extraction process of 5 min for each cycle was chosen over a single extraction cycle in 25 min. The resulting corn starch produced by UAE could maintain the low viscosity even in high temperatures. Hence, apart from accelerating the extraction, UAE was also useful to modify the starch characterization. Moreover, the proposed method demonstrated a green extraction procedure, as there was no presence of any additional organic solvent.

1. Introduction

Corn (Zea mays) is one of the essential commodities in the agricultural sector. In Indonesia, corn productivity is the second-highest after rice [1,2]. The world's need for corn is not limited to fresh products only, but also its derived products such as dry corn, cornflour, and corn starch. These products form of corn is preferable because the fresh form of corn has a short shelf-life. The highest market demand for corn, both domestic and international, is in the form of starch, which can reach 74% of the material's dry weight [3–5]. In the food industry, starch is widely used for sweetener, gelling agent, thickener, coating, and texture forming. Meanwhile, the non-food industries utilize starch for the production of textile, glue, medicine, bioethanol, and other products [5–8].

Several conventional extraction methods exist, and maceration is one of the most common methods used by industries. However, this method requires a long processing time and produces a low yield [9]. Various alternative methods that are faster and environmentally friendly has been proposed to overcome the issues, including ultrasound-assisted extraction (UAE). UAE can increase the mass transfer of starch granule, which is trapped by protein and cellulose fibers bound with pectin in the cell walls [10], into the medium by its cavitation effect. The proposed mechanism from the ultrasonic waves causes a cell break down, resulting in the analyte's secretion and faster extraction time.

However, to achieve the maximum extraction yield, several factors affecting UAE efficiency need to be optimized, i.e., ratio solvent to sample, cavitation cycle, power, and time. It can be done by applying chemometrics, namely Box-Behnken Design (BBD), in conjunction with Response Surface Methodology (RSM). Following the optimization of the extraction condition, the starch's quality obtained by the proposed method was evaluated, viz. starch content, size particle, viscosity, and starch granule.
2. Materials and Methods

2.1. Sample Collection

The study used two different corn samples. In the optimization step, the corn BISI-2 Yellow Hybrid was supplied by a farmer in Yogyakarta. For the characterization, the sample was collected by random sampling from several local markets in Yogyakarta. The sample was obtained in the dried form then manually sorted to remove dirt. After that, the corn was ground into powder. The cornflour was then stored in a packed plastic with silica gel.

2.2. Sample Extraction

Ultrasound-assisted extraction was performed using an ultrasonic probe UP200St 200 W, 26 kHz (Hielscher, Germany). Corn flour was weighed 15 g and placed in a beaker. Subsequently, 0.1% NaOH solution was added as a solvent. The mixture was then extracted for 10 min. To determine the effect of the extraction factor on efficiency and to obtain the optimum extraction conditions, various extraction variables were evaluated, including power ($x_1$, 30-90%), cavitation cycle ($x_2$, 0.3-0.9 s$^{-1}$), and solvent to sample ratio ($x_3$, 10:1-30:1 g ml$^{-1}$). The resulting solution was then filtered to remove the solid material. The extract was deposited, and the sediment was transferred in a petri dish to dry in a cabinet dryer (50 °C) for 24 h. The dried precipitate was corn starch obtained from the extraction process. The corn starch obtained is then ground into a powder form. The starch yield obtained was calculated based on the following equation:

\[
\text{Starch yield (\%)} = \frac{w_1}{w_2} \times 100
\]

where $w_1$ is the sample weight, and $w_2$ is the weight of starch extracted by UAE.

2.3. Design of Experiment

Box-Behnken Design (BBD) was used as an experimental design to evaluate the independent variables affecting the extraction process. Following this, the optimization was conducted using Response Surface Methodology (RSM). Each variable had a different unit and level range, therefore to get a uniform response, the levels were normalized with a range of -1 to +1. Table 1 shows the list of the independent variables and their level. The whole design was presented in Table 2, consisting of 15 experimental runs performed in random orders and duplication.

| Variable                  | Code | -1 | 0  | +1 | Unit       |
|---------------------------|------|----|----|----|------------|
| Power                     | $x_1$| 30 | 60 | 90 | %          |
| Cavitation cycle          | $x_2$| 0.3| 0.6| 0.9| s$^{-1}$   |
| Solvent to sample ratio   | $x_3$| 10:1|20:1|30:1|g sample/ml solvent|

The responses obtained on the starch yield were then evaluated as the basis for developing a mathematical model with a second-order polynomial function,

\[
y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \epsilon
\]  

(1)

where $x_1, x_2, \ldots, x_k$ is the UAE factor affecting the efficiency of the extraction process, $y; \beta_0, \beta_i (i = 1, 2, \ldots, k), \beta_{ij} (i = 1, 2, \ldots, k; j = 1, 2, \ldots, k)$ are an unknown parameter, and $\epsilon$ is a random error.
Table 2. Box-Behnken design for three factors with observed responses.

| Run | x₁ | x₂ | x₃ | Relative value to the max. yield (%) | Run | x₁ | x₂ | x₃ | Relative value to the max. yield (%) |
|-----|----|----|----|-------------------------------------|-----|----|----|----|-------------------------------------|
| 1   | 1  | -1 | 0  | 50.46                               | 16  | 1  | 0  | -1 | 89.06                               |
| 2   | -1 | 1  | 0  | 44.13                               | 17  | 1  | 0  | 1  | 90.45                               |
| 3   | 1  | 1  | 0  | 93.60                               | 18  | -1 | -1 | 0  | 50.35                               |
| 4   | 1  | 0  | 1  | 89.63                               | 19  | 0  | 0  | 0  | 82.61                               |
| 5   | -1 | 0  | -1| 36.89                               | 20  | 1  | -1 | 0  | 45.65                               |
| 6   | 0  | 0  | 0  | 66.31                               | 21  | 1  | -1 | 1  | 53.82                               |
| 7   | 0  | 1  | 1  | 100.00                              | 22  | -1 | 0  | 1  | 59.95                               |
| 8   | 0  | -1 | 1 | 55.49                               | 23  | 0  | 0  | 0  | 58.70                               |
| 9   | 0  | 0  | 0  | 78.28                               | 24  | 0  | -1 | 1  | 54.74                               |
| 10  | -1 | -1 | 0 | 55.41                               | 25  | 0  | 1  | -1| 58.50                               |
| 11  | 0  | 1  | -1| 71.49                               | 26  | 0  | 0  | 0  | 71.61                               |
| 12  | 0  | -1 | -1| 55.87                               | 27  | 1  | 1  | 0  | 100.00                              |
| 13  | -1 | 0  | 1 | 83.69                               | 28  | 0  | 1  | 1  | 96.77                               |
| 14  | 0  | 0  | 0  | 90.02                               | 29  | 0  | -1 | -1| 56.72                               |
| 15  | 1  | 0  | -1| 95.12                               | 30  | -1 | 0  | -1| 47.17                               |

The construction and analysis of the experimental design and the response surface to reach the optimum conditions were performed using STATGRAPHICS Centurion XVI (Statpoint Technologies, Inc., USA). This statistical tool utilized the quadratic model equation to build response surfaces. The Analysis ToolPak of an Excel of Microsoft Office Professional Plus 2013 was used to analyze the experimental data generated from single-factor experiments. The Analysis of Variance (ANOVA, \( p = 0.05 \)) was used to determine the significance of the effect of studied variables. If ANOVA suggested a significant difference, the Least Significant Difference (LSD, \( p = 0.05 \)) test was used to check the differences among the means.

2.4. Model Validation
The model obtained at the optimization stage was evaluated for its suitability towards the process based on the lack-of-fit value, the standard error, and the coefficient of determination \( (R^2) \). The lack-of-fit test is designed to determine the adequacy of the selected model in describing the observed data, or a more complex model is required. The model is stated to have high compatibility, given the \( p \)-value of the ANOVA is higher than 0.05. Additionally, the standard error value is used to measure the variation in estimation statistically.

2.5. Kinetics and extraction cycle
The study was conducted by varying the extraction time (5-30 min) using a randomized block design with duplication. However, to obtain the best extraction procedure, a comparative study of the extraction cycle was performed.

2.6. Starch Characterization
The evaluation parameters of starch were starch content using DNS (3,5-dinitrosalicylic acid) method, starch fineness, viscosity using Rapid Visco Analyzer (RVA) 4500 (Perten, Sweden), and starch granule which were carried out under a microscope with a magnification of 200× and 400×.
3. Results and Discussion

3.1. Evaluation of extraction factors on starch yield

Variables that likely to affect UAE for corn starch extraction were studied, including power ($x_1$, 30-90%), cavitation cycle ($x_2$, 0.3-0.9 s$^1$), and solvent to sample ratio ($x_3$, 10:1-30:1 g ml$^{-1}$). BBD was used to determine the effect of process variables and the interactions between these variables and their response. The response was expressed as the relative value to the maximum extraction yield (%), as shown in Table 2.

The responses obtained after extraction of the experimental design was calculated to obtain a mathematical model. ANOVA was used to determine each effect's statistical significance by comparing the mean square against an estimate of the experimental error. Figure 1 shows the standardized effect ($p<0.05$) of each factor importance plotted in a Pareto chart.

A bar crossing a vertical line corresponds to a factor or combination of factors that significantly affect the response. Two main variables, power ($x_1$) and cavitation cycle ($x_2$), significantly affected the extraction yield. Increasing these values would result in the improvement of the starch yield. The same trend would also be found with the combination variable of both variables. A study conducted by Carrera et al. [11] and Suhaimi et al. [12] showed that power is a variable that affects cavitation occurrence. The greater the power, the faster the ultrasonic wave propagation process in the medium.

3.2. The prediction capability of the regression model

Based on the ANOVA, all variables were used to evaluate the fitting properties for the model. A quadratic polynomial regression model (Equation 2) was generated, which described the relationship between the starch yield and the three variables:

$$y = 74.58 + 13.91 x_1 + 12.10 x_2 + 7.49 x_3 - 3.81 x_1 x_1 + 13.16 x_1 x_2 - 7.96 x_1 x_3 - 9.11 x_2 x_2 + 8.64 x_2 x_3 + 3.22 x_3 x_3$$

(2)

where $y$ is the extraction yield and $x_1$ ($x_1$, power; $x_2$, cavitation cycle; $x_3$, ratio solvent to sample).

A lack-of-fit test is carried out to determine whether the model can describe the observed data or a more complex model is required. The lack-of-fit test showed a higher value than 0.05 (0.9478); hence the model could explain the observed data at the 95% confidence level. A comparison between the
3.3. Optimization of Extraction Condition

From the model obtained, a three-dimensional response surface plot was constructed. Figure 2 illustrates the relationships between the response value (y, response) and the independent variables (x₁, power; x₂, cavitation cycle; and x₃, solvent to sample ratio). The optimum response (110.91%) can be achieved by the ultrasonic power of 87%, cavitation cycle of 0.9 s⁻¹, and ratio solvent to sample 30:1 g ml⁻¹. However, a further optimization for the cavitation cycle was employed to know whether the maximum designed value is sufficient or a higher level is needed. The maximum cavitation produced by the equipment (1 s⁻¹) resulted in a higher response by 100% and 76.67% for the 0.9 s⁻¹. Therefore, the power of 1 s⁻¹ was chosen as the optimum level. Although the solvent to sample ratio has also resulted in the maximum design level, no further optimization was conducted from an economic perspective. Additionally, compared with the study by Suarni et al. [13], the proposed method demonstrated a safer and more environmentally friendly approach without the presence of any additional organic solvent.

3.4. Kinetic Study

The kinetics assessment was conducted by varying the extraction time between 5 and 30 min. Figure 3 illustrates that the response was increasing until a plateau was reached at 25 min. A comparative study by shortening the extraction time to 5 min for two-extraction cycles was conducted. The result showed that a 2-extraction cycle of 5 min extraction produces the same yield as the 1-extraction cycle for 25 min. Since the purpose was to develop an efficient UAE method, a lower processing time and energy were desired. Therefore, the two-extraction cycle of 5 min was chosen as the optimum extraction time.

3.5. Characterization of starch extracted by UAE

3.5.1. Viscosity

Viscosity serves as one of the most important characteristics of starch. Figure 4 shows the viscosity of the corn starch produced by UAE and commercial starch. The peak viscosity, holding viscosity, and the final viscosity of the UAE corn starch was lower than those of the commercial sample. This result was in accordance with the study of several researchers using different samples. Zuo et al. [14] and Luo et al. [15] found a decrease in rice and corn starch viscosity, respectively, after ultrasound treatment. Another study conducted by Sujka and Jamruz [16] also found a viscosity decrease after ultrasonication in potato, corn, wheat, and rice starch.
Figure 4. Viscosity comparison of corn starch produced by UAE and commercial corn starch.

The starch content for the UAE produced starch was 73% and the commercial starch was 89%. The starch content of the cornflour was 64%. The amount of starch extracted using the proposed method was 27%. This result shows an enhancement to the studies by other researchers. The study conducted by Sit et al. [17] taro (Colocasia esculenta) starch extraction by UAE can only be extracted a maximum of 19% while Gonzales-Lemus et al. [18] extracted starch from jicama tuber with 23% of yield.

3.5.2. Granule characteristics
Starch granule observation was conducted using an electron microscope. Figure 5 shows that starch treated with ultrasound produced a lot of smaller granules. Other than that, ultrasound produced starch seemed to have more damage granule compared to the commercial starch. The disruption of the granule, either pores, cracks, or holes, shows benefit in starch modification. More open granules enhanced the chemical reaction by increasing the penetration of the chemical agent and catalyst [19]. Enzymatic modification is also benefited by the starch granule disruption, as the enzymes are easily penetrated to the granules [20]. Thus, the disrupted starch granules are beneficial to speed up the modification process.

Figure 5. The microscopic appearance of ultrasound produced corn starch (UCS) and commercial corn starch (CCS).

4. Conclusion
Ultrasound-assisted extraction (UAE) for corn starch production was developed in the present study. Combining BBD and RSM, the optimum UAE condition for corn starch was achieved, power of 87%, cavitation cycle of 1 s⁻¹, and solvent to sample ratio of 30:1 g ml⁻¹. Following these conditions with a two-extraction cycle of 5 min, each produced the optimum starch yield. Finally, the evaluation of the starch quality after the ultrasound application resulted in 73% of starch content, and smaller granules were found with more disrupted granules than the commercial corn starch, resulting in lower viscosity. However, in addition to accelerating the extraction process, UAE also advantageous in starch...
modification. Furthermore, the limitation in organic solvent usage in the proposed procedure indicating a safe and environmentally friendly method for corn starch extraction using UAE.

5. Reference

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