Optimization of pectin and citric acid concentration on the physical and organoleptic characteristics of Barhi date jam using response surface methodology

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Abstract. Date is a tropical plant originating from Middle East. Among various types of dates in the world market, Barhi is the most famous one as its edibility during all stages of maturity. Barhi date has a short ripening stage, therefore further processing is needed to extend its shelf life. One of them is by processing the Barhi dates into a jam. The aim of this study was to determine the optimum formulation of the jam. The optimization method was using Response Surface Methodology with Centre Composite Design and two independent variables, i.e., pectin and citric acid concentration and the responses are total colour difference (ΔE) and spreadability. The optimum formulation of Barhi date jam was 0.52% pectin and 0.69% citric acid. It had total colour difference (ΔE) of 6.77 and spreadability of 9.2 cm. The results of the actual data verification and the predicted value of the software showed no significant difference (p-value> 0.05). The results of quality acceptance test showed that Barhi date jam can be accepted by consumers.

1. Introduction
Date (Phoenix dactylifera L.) is a type of palm plant that is widely grown in Middle East countries. According to FAO, in 2018, the top 3 countries as the largest producer of dates are Egypt (1.5 million tons), Saudi Arabia (1.3 million tons) and Iran (1.2 million tons) [1]. In the same year, Indonesia became the sixth date importer country in the world with a total import of 39907 tons [2]. In contrast, Indonesia does not produce date despite Indonesia as a tropical country with a high humidity can be a potential land for date plantation [3]. Date plantation can be used as an alternative farming business, tourism and ornamental plants [4].

There are different varieties of dates in the market. Barhi or Barhee is one of the most popular date varieties because its uniqueness compared to the other varieties. It can be consumed at all mature stage while the other is consumed at ripening stage. Basically, date is a climacteric fruit that it can be ripen after harvested. Barhi date has short ripening stages therefore further processing is necessary to extend its shelf life. One of the food processing that can be done is making it into jam.

Jam is a semi-wet product made from processed fruits with a mixture of sugar, pectin, citric acid, water and permitted food additives [5]. The selection of pectin and citric acid concentration is an important consideration because it will affect the physical characteristics of the jam. The texture of the jam is formed due to the formation of a gel complex between the addition of pectin-sucrose-citric acid [6]. The optimum or ideal concentration of pectin for gel formation is 0.75-1.5% [7]. Pectin is
necessary to form a jam structure, if the pectin is too low then it cannot form a gel because it is too
diluted and when the pectin is too high it will form a hard, strong and steady gel. The addition of citric
acid concentrate that produces jam quite well is 0.5%. Meanwhile, the optimum condition for citric
acid is on pH 3.2%-3.4% [8].

In the making of jam, suitable formulation is important to produce an ideal and optimum jam,
therefore optimization of the formulation of Barhi date jam is needed. The optimization method used
is Response Surface Methodology (RSM) with Central Composite Design (CCD) with two
independent variables, i.e., pectin concentration and citric acid concentration. In the other hand, a
related study is still limitedly published so it is necessary to get optimal condition in order to obtain
the best characteristics of Barhi date jam.

2. Materials and methods

2.1. Materials

Materials used in this study was Barhi Dates from Jordan supplied by Madrasah Putri At-Taqwa
Karanganyar, Central Java. Sugar, mineral water and bread obtained from local supermarket. Pectin,
citric acid, pH buffer powder, and sterile distilled water obtained from CV Makmur Sejati.

2.2. Methods

The study used Response Surface Methodology (RSM) with Central Composite Design (CCD) in the
Design Expert 9 program with 2 independent variables, i.e., pectin and citric acid concentration. Total
run was 13 with 5 centre points. The central composite design is shown in Table 1. The observed
responses are total colour difference and spreadability.

| Table 1. Independent variables design and level in central composite design |
|---------------------------------------------------------------|
| Independent variables (%) | Symbol | Range & level |
|---------------------------|--------|---------------|
| Pectin concentration      | X1     | 0.5           | 1              |
| Citric acid concentration | X2     | 0.5           | 1              |

The research consisted of two stages, preliminary and main research. Preliminary research aimed to
determine the limits of the independent variables and the formulation in making Barhi date jam
(concentration of pectin, citric acid, sugar and weight of dates). In preliminary research, formulations
were obtained as a reference for the making of date jam. For the main research, it aimed to determine
the optimum point of the 13 experiment that had been designed using CCD DX 9 which produced the
best response. Observation of physical characteristic was done for Barhi date as raw material and its
jam. Physical characteristic observed in Barhi date was colour measurement by using Colour Grab
Application and visually, pH [9] and total soluble solid (°Brix) [10] while for the Barhi date jam were
total colour difference (Colour Grab Application) and spreadability [11]. Organoleptic responses also
were observed by using quality acceptance test [12].

Data analysis used the Central Composite Design with DX 9 including model selection, Analysis of
Variance (ANOVA), Model Equations, Response Surface Curve and optimization of Barhi date jam
formulation based on the highest desirability value. Furthermore, it was analysed by using Minitab 18
Statistical Software (Minitab Inc., State College, Pennsylvania, USA) for Paired T-Test in order to
compare the optimum process in Design Expert 9 prediction with verification result of total colour
difference and spreadability.
3. Results and discussion

3.1. Raw materials characterization

The physical characteristic of Barhi date can be seen in Table 2.

| Parameter                  | Result        | Literature    |
|----------------------------|---------------|---------------|
| pH                         | 6.7 ± 0.7     | 7-7.2 [13]    |
| Total Soluble Solid (°Brix)| 32            | 35 [14]       |
| Colour                     |               |               |
| L* (Lightness)             | 42.72 ± 2.15  | 68.35 [15]    |
| a* (redness)               | 17.94 ± 0.18  | 10.87 [15]    |
| b* (yellowness)            | 48.84 ± 1.66  | 48.44 [15]    |
| Visual                     | Orange-chocolate (bright) | Orange-chocolate (bright) [14] |

Notes: Data mean ± standard deviation (n=3)

Based on Table 2, the pH of Barhi dates was 6.7. According to the literature, Barhi date had a pH ranging from 7-7.2 [13]. Total soluble solid of Barhi date was 32 while according to the literature was 35 [14]. Total soluble solid can be used to identify the level of fruit maturity, the riper the fruit, the higher the value of total soluble solid contained therein.

The obtained value (Table 2) for lightness was 42.72, redness was 17.94 and yellowness was 48.84. While visually it had yellow, orange-brownish colour. Barhi dates had three stages of maturity namely; Khalal, Rutab and Tamer [14]. At Khalal stage, the fruit had bright yellow or red colour. After Khalal, the fruit skin turned into brown colour in Rutab stage. In Tamer stage as the last stage of maturity, Barhi date was fully ripe. Barhi date is widely consumed at Khalal stage where the fruit is crispy and reaches it maximum weight and size.

3.2. Formulation optimization with response surface methodology

Experimental design and result of total colour difference and spreadability can be seen in Table 3.

| Std | Run | Factor 1        | Factor 2 | Response 1 Total colour difference (ΔE) | Response 2 Spreadability (cm) |
|-----|-----|-----------------|----------|----------------------------------------|--------------------------------|
| 1   | 13  | 0.5             | 0.5      | 6.74                                   | 8.30                           |
| 2   | 3   | 1               | 0.5      | 5.23                                   | 7.20                           |
| 3   | 9   | 0.5             | 1        | 7.32                                   | 7.80                           |
| 4   | 10  | 1               | 1        | 6.74                                   | 6.70                           |
| 5   | 1   | 0.4             | 0.75     | 4.84                                   | 9.00                           |
| 6   | 2   | 1.1             | 0.75     | 6.32                                   | 8.00                           |
| 7   | 5   | 0.75            | 0.4      | 7.33                                   | 8.50                           |
| 8   | 7   | 0.75            | 1.1      | 8.70                                   | 7.30                           |
| 9   | 11  | 0.75            | 0.75     | 7.20                                   | 8.70                           |
| 10  | 6   | 0.75            | 0.75     | 7.55                                   | 8.50                           |
| 11  | 12  | 0.75            | 0.75     | 8.00                                   | 9.00                           |
| 12  | 4   | 0.75            | 0.75     | 8.13                                   | 9.50                           |
| 13  | 8   | 0.75            | 0.75     | 8.65                                   | 9.60                           |
Model analysis results for total colour difference and spreadability response can be seen in Table 4.

**Table 4.** Model analysis and analysis of variance (ANOVA) results for response

| Response           | Model    | Equation                                                                 | Significancy (p<0.05) | Lack of fit (p<0.05) | R²  |
|--------------------|----------|--------------------------------------------------------------------------|------------------------|----------------------|-----|
| Total colour       | Quadratic| \(Y_1 = -2.79444 + 26.86352(X_1) - 0.34426(X_2) + 3.72000 - 19.76800 - 0.28800\) | 0.0278                 | 0.1947               | 0.7834 |
| difference         |          |                                                                         |                        |                      |     |
| Spreadability      | Quadratic| \(Y_2 = +0.53673 + 9.11289(X_1) + 16.77147(X_2) - 8.58180E-014 - 7.28000 - 12.08000\) | 0.0279                 | 0.3226               | 0.7834 |

Based on Table 3, it can be seen that the highest total colour difference (\(\Delta E\)) was obtained from the addition of 0.75% pectin and 1.1% citric acid, while for the lowest total colour difference (\(\Delta E\)) was obtained from the addition of 0.4% pectin and 0.75% citric acid. The highest spreadability is 9.6 cm which was obtained from the addition of 0.75% pectin and 0.75% citric acid, while the lowest spreadability is 6.7 cm which was obtained from the addition of 1% pectin and 1% citric acid.

The results from analysis of variance (ANOVA) (Table 4) shows that the model selected for both responses was quadratic. The selection of models based on p-value <0.05 P-value less than 5% indicated that the model exerts a significant influence on the response, meaning that the model was acceptable [16]. The lack of fit tests with p-value >0.05 was 0.1947 for total colour difference and 0.3226 for spreadability. Lack of fit tests or insignificant model inaccuracies were a requirement for good models due to the suitability of response data with suggested models [17]. The R² or determination coefficient indicated the rate of correlation between variables in the response to the model. The R² value for colour was 0.7834 and for spreadability was 0.7832. That means 78.34% and 78.32% of the actual data can be explained by the model. R² value approaching 1 means that data between variables or factors and responses has a high correlation rate between those presented in the model [18].

### 3.3. Total colour difference response analysis

RSM equation for formulation optimization of *Barhi* date jam with total colour difference as a response is:

\[
Y_1 = -2.79444 + 26.86352(X_1) - 0.34426(X_2)
\]  

(1)

**Note:**  
*Y₁*= Total Colour Difference Response (%)  
*X₁*= Pectin Concentration (%)  
*X₂*= Citric Acid Concentration (%)

The equation shows that the interaction of pectin and citric acid concentration was suitable and it could improve the colour response in *Barhi* date jams desired. The interaction of the addition of citric acid in a small amount could decrease the colour response of the jam, thus the colour was pale.

The addition of pectin in a big amount could decrease the brightness of the jam, because high concentration of pectin would form a tight matrix that caused the jam become darker [19]. The addition of citric acid in a big amount caused the jam become bright or the original colour of dates could be maintained. Citric acid serves as an acid that not only strengthens the taste but also brighten jam colour and clears the formed gel [20]. In addition, the colour produced by jam also depends on the level of maturity of the fruit used. If *Barhi* date used was at immature stage, the colour of the jam will be pale yellow and if the date used was fully riped, the colour of the jam will be dark brown.

Contour plot graphic in Figure 1a is showing the colour response was influenced by two significant factors, pectin and citric acid concentration.
Figure 1. (a) Contour plot (b) 3D total colour difference responses.

The different colours on the plot contour chart shows the colour response values. The green-yellowish colour indicated the lowest total colour difference (ΔE) response value of 4.84. The yellow-orange colour indicated the highest ΔE response of 8.70. The optimum value for the colour response was located in an orange-yellow area marked with a red dot. The surface shape of the interaction between components can be seen in the 3D graph (Figure 1b). The lowest area showed the lowest response value and the highest area indicated the highest response value. The yellowish-green 3D curve was the minimum point area while the yellow-orange curve was the maximum point.

3.4. Spreadability response analysis

RSM equation for formulation optimization of Barhi date jam with spreadability as a response is:

\[ Y_2 = +0.53673 + 9.11289X_1 + 16.77147X_2 \]  

Note: \( Y_2 \) = Spreadability (%)  
\( X_1 \) = Pectin Concentration (%)  
\( X_2 \) = Citric Acid Concentration (%)

The equation shows that the interaction of pectin and citric acid concentration were suitable and could improve the spreadability response in Barhi date jam. The higher the amount of pectin added, the higher the spreadability value of the jam, but the consequences are it will be hard, thick gel texture with short spreadability. Meanwhile, the addition of pectin in a small amount would cause the gel texture cannot be formed and the spreadability would be short [21].

According to the literature, pectin is a colloid that has a negative charge [22]. Pectin will clot and form fine fibres. This structure is able to hold liquid. The addition of citric acid in a big amount would decrease the spreadability response because the texture was runny and the spreadability was short [21]. Citric acid with a pH that is too acidic would give rise to H + ions [23]. These ions could cause syneresis, the discharge of water from the gel so that the thickness of the jam will decrease or even not form [24]. The addition of sugar concentration will affect the balance between pectin and water and can reduce the stability of excess pectin in forming fine fibres, so that the gel that is formed is not too hard and thick, causing the resulting spread of jam to be longer.

Contour plot graphic in Figure 2a showing the colour response was influenced by two significant factors, pectin and citric acid concentration.

The different colours on the plot contour chart shows the spreadability response values. The greenish colour indicated the lowest spreadability response value of 6.7 cm. The yellow-orange colour indicated the highest spreadability response of 9.6 cm. The optimum value for the spreadability response was located in an orange area marked with a red dot. The surface shape of the interaction
relationship between components can be seen in the 3D graph (Figure 2b). The low area showed the lowest response value and the high area indicated the highest response value. The yellowish-green 3D curve was the minimum point area while the yellow-orange curve was the maximum point.

![3D graph](image)

**Figure 2.** (a) Contour plot (b) 3D spreadability responses.

### 3.5. Verification of formulation optimization for Barhi date jam

Optimization was done after the mathematical model is obtained for each response. The optimization process was used to get the best combination of formulation. Importance level started from positive 1 (+) to positive 5 (+++++). The more plus (+) signs, the higher the level of importance of the attributes/responses measured against the response. Based on the criteria of interest level, concentration of pectin and citric acid was a component optimized with importance level of moderate (+++). It was because of pectin and citric acid will affect the jam.

DX 9 would process all response variables based on the established criteria and provide several solutions as the selected Barhi date jam formulation. The value of optimization targets that can be achieved is called desirability. Desirability has a value of 0 to 1. The higher the complexity of the test variable and the optimization target value, the harder it is to achieve a desirability value close to one [25]. According to the literature, the desirability value on the scale of 1.00-0.80 indicates an excellent number because the response value is already ideal and acceptable. Because the purpose of optimization was not to obtain a desirability value of 1 but for the best or optimum conditions [26]. The verification result of Barhi date jam can be seen in Table 5.

| Table 5. The result of verification |
|-----------------------------------|
| Factor                          | Response |
| Pectin (%) | Citric acid (%) | Total colour difference (ΔE) | Spreadability (cm) |
| Predictions  | 0.18 | 0.685 | 6.770 | 9.125 |
| Verification* | 0.52 | 0.69 | 6.73 | 9.2 |
| p-value | 0.615 | 0.583 |

Table 5 shows that Barhi date jam has a total colour difference ΔE of 6.73 and a spreadability of 9.2cm. The verification result had a value close to the predicted results. This demonstrated the optimum formulation for the making of Barhi date jam in accordance with recommendation by Design Expert 9 program. The results of verification and prediction then continued with the Paired t-Test using Minitab 18. Based on the results of the Paired t-Test, the p-value generated by each response has a value of >0.05. P-value more than 0.05 (5%) showed that the predicted and verification values were
not significantly different, thus it indicated the accuracy of the model or prediction supports the verification results [27].

3.6. Quality acceptance test
This test was based on the assessment of panellist who will assess the quality of a product in the form of like or dislike. It is carried out by 60 - 100 untrained panellists [12]. Panellists express their personal preference subjectively regarding sensory characteristics or quality of the product. The purpose of the acceptance test is to find out whether a new product with particular sensory characteristics is acceptable to the public or not, but it cannot be used to foresee the acceptance in the marketing [28]. This test was involving 40 untrained panellists and they were asked to filling yes or no form in terms of colour, aroma, texture and overalls of Barhi date jam.

For colour, out of 40 panellists, 77.5% liked and the remaining 22.5% disliked. 31 panelists liked the colour of the jam, while 9 panellists disliked the colour. For aroma, 92.5% of the panellists liked the jam while the remaining is disliked. For texture, 100% of the panellists liked the texture. So it could be conclude that all the quality parameter of the jam was acceptable for the majority of the panellists.

4. Conclusions
Optimum formulation of Barhi date jam was the addition of pectin concentration of 0.52% and citric acid 0.69%. It resulted in total colour difference value of 6.77 and a spreadability of 9.2 cm. Verification results and prediction values showed that there was no significant difference (p-value >0.05). The percentage of quality acceptance tests showed that Barhi date jam was acceptable for the majority of the panellists. The addition of pectin and citric acid in a high amount would increase the total colour difference and spreadability value but it would decrease after reaching the optimum point.

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