Optimization of pyrolysis condition for bioactive compounds of wood vinegar from oil palm empty bunches using response surface methodology (RSM)

H A Oramahi¹, Elvi Rusmiyanto P. Wardoyo²,³ and Kustiati²

¹ Faculty of Forestry, Universitas Tanjungpura, Jalan Prof. Dr, Hadari Nawawi, Pontianak, West Kalimantan 78124, Indonesia
² Faculty of Mathematics and Natural Sciences, Universitas Tanjungpura, Jalan Prof. Dr, Hadari Nawawi, Pontianak, West Kalimantan 78124, Indonesia

E-mail: elvirusm1971@gmail.com

Abstract. Optimized of the phenol and acid total of wood vinegar from oil palm empty bunches using response surface methodology was carried out. Response surface methodology (RSM) with central composite design (CCD) was employed to optimize the parameters of pyrolysis process, namely pyrolysis temperature ($X_1$) and pyrolysis times ($X_2$). Two variables, namely pyrolysis temperature (°C) and pyrolysis time (min) with 5 levels (-1.414, -1, 0, 1 and 1.414) were used to design the optimization model. The two variables, a temperature of 420 °C and a pyrolysis temperature of 122.40 minutes were the optimized conditions for the response variables of phenol total content. Meanwhile, the temperature of 422 °C and the pyrolysis temperature of 118.5 minutes were the optimized conditions for the response variables of the total acid content. The regression equation obtained for phenol and acid total content were $Y = 2.97 + 0.12 X_1 + 0.03 X_2 + 0.23 X_1^2 - 0.24 X_2^2 + 0.24 X_1X_2$, and $Y = 9.89 + 0.63 X_1 + 0.70 X_2 - 0.56 X_1^2 + 0.12 X_2^2 - 1.70 X_1X_2$, respectively. The optimal conditions for the highest yield of phenol and acid total were 3.13 and 10.04 %, respectively.

1. Introduction
Wood vinegar prepared from many different sources of wood have been use as safe natural inhibitors with various applications, such as antifungal, antimicrobial, and antioxidant activities [1, 2, 3]. Wood vinegar obtained from pineapple plant waste biomass has been reported possessing antioxidant activity, and rich of phenolic compounds especially guaiacol, catechol, methoxy catechol and syringol [4]. Wood vinegar, also called liquid smoked, a yellowish or dark brown condensate made from wood carbonization process at a high temperature in the absence of oxygen [5].

Various studies about a different kind of wood, pyrolysis temperature, and temperature time for the wood vinegar yield and bioactive compound have been published. The temperature of pyrolysis and types of wood are dominant factor for yield of wood vinegar and bioactive component of wood vinegar including phenol and phenolic compounds [6, 7]. For example, the highest yield of phenol and phenolic compound in wood vinegar made from palm kernel shells was about 70% area with increasing temperature up to 475 °C [7].
Response surface methodology (RSM) approach succeeded in optimizing the extraction conditions of the phenolic for antioxidants from the fruits of *Euterpe oleracea* [8] and *Artemisia absinthium* [9]. Optimization of operating parameter extraction of antioxidant from *Coriandrum sativum* seeds was studied [10] and it was found that optimum condition of subcritical water extraction was obtained at temperature of 200 °C, pressure of 30 bar and extraction time of 28.3 min.

However, it has not previously been used to optimization of bioactive compound including phenol and acid total in wood vinegars made from oil palm empty bunches. The aim of the study is to develop a maximum yield of phenol and acid total of wood vinegar from oil palm empty bunches.

2. **Materials and Methods**

2.1. **Pyrolysis of wood vinegar**

Wood vinegar was produced from burning wood particles of oil palm empty bunches. The material was collected from Bumi Pratama Khatulistiwa (BPK) Ltd. and was converted into particle with a disk mill, and air dried of moisture content (12.0%). The pyrolysis process was conducted at the Engineering Laboratory, Faculty of Agriculture Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia.

2.2. **Analysis of phenol total**

Phenol total of wood vinegar from oil palm empty bunches was calculated by using the method of spectrochopy [11]. Wood vinegar (1mL) was diluted 1.000 times. One mL of the diluted sample was put into 5 mL 2% Na$_2$CO$_3$ solution. After 10 minutes, 0.5 mL of Folin Ciocalteau suspension was added to the solution. Absorbance of the solution at 750 nm was measured by a UV-Vis spectrophotometer (Shimadzu 1601, Shimadzu Manufacturing Co. Ltd, Japan). The phenol total content in each wood vinegar was measured by comparing with that of pure phenol suspension.

2.3. **Analysis of Acid Total**

The acidity of the wood vinegar was calculated using the method of AOAC [12]. Wood vinegar (1 mL) was diluted to 100 mL with deionised (DI) water. The 3 drops PP (Phenolphthalein) indicator was added into it, and the solution was titrated by 0.1 N NaOH.

2.4. **Experimental Design**

CCD was applied to optimize phenol and acid total content made from oil palm empty bunches. Operation condition process including pyrolysis temperature ($X_1$) and pyrolysis time ($X_2$) were the selected independent variables (table 1).

| Independent Variable | Symbol | -\(\alpha\) (-1.44) | -1 | 0 | 1 | +\(\alpha\) (1.44) |
|----------------------|--------|----------------------|-----|---|---|---------------------|
| Temperature of pyrolysis (°C) | $X_1$ | 329.30 | 350 | 400 | 450 | 470.70 |
| Times of pyrolysis (min) | $X_2$ | 98.79 | 105 | 120 | 135 | 141.21 |

These variables were low and high factor settings are coded as -1 and 1, the midpoint coded as 0. The factor settings of trails that run along axes drawn from the middle of the cube through the centers of each face of the tube are coded as -1.414 or 1.414, and total of 13 experimental runs.

For optimum point prediction, second-order polynomial equation is following:

$$ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon $$ (1)
where $\beta_0$, $\beta_1$, $\beta_2$, and $\beta_3$ are the regression coefficients for intercept, linear, quadratic and interaction terms, respectively, and $x_i, x_j$ are the independent variables [14].

2.5. Statistical analysis
SAS software (version 8.2, SAS Institute Inc., NC. USA) were used for the analysis of the central composite design.

3. Results and Discussion

3.1. Maximizing the phenol total content of wood vinegar
For determining the temperature pyrolysis ($X_1$), and times of pyrolysis ($X_2$) within the range of 329.30-470.70 °C, and 98.79-141.21 minutes, respectively, the trials were designed based on a CCD. The phenol total compounds of wood vinegar from oil palm empty bunches was further optimized using RSM [13]. Two factor levels in coded and un-coded values are shown in table 1. The experimental design and the observed data for phenol total content is shown in table 2.

Table 2. Real value of variables and response variable of central composite design

| Run | Temperature ($^\circ$C; $X_1$) | Times (min; $X_2$) | Responses |
|-----|--------------------------------|--------------------|-----------|
| 1   | 350 a (-1)b                     | 105a (-1)b         | 1.72      |
| 2   | 350 (-1)                        | 135 (1)            | 2.64      |
| 3   | 450 (1)                         | 105 (-1)           | 3.16      |
| 4   | 450 (1)                         | 135 (1)            | 3.10      |
| 5   | 400 (0)                         | 120 (0)            | 3.11      |
| 6   | 400 (0)                         | 120 (0)            | 3.03      |
| 7   | 400 (0)                         | 120 (0)            | 2.72      |
| 8   | 400 (0)                         | 120 (0)            | 2.64      |
| 9   | 400 (0)                         | 120 (0)            | 3.28      |
| 10  | 470,70 (1.414)                  | 120 (0)            | 3.51      |
| 11  | 329,30 (-1.414)                 | 120 (0)            | 4.06      |
| 12  | 400 (0)                         | 141,21(1.414)      | 2.88      |
| 13  | 450 (0)                         | 98,78 (-1.414)     | 3.33      |

Where: a) Condition of treatment and b) Code

Some factors contribute to maximizing the phenol and phenolic compound of wood vinegar were temperature, feed size and feed rate [7, 15]. Similar results were obtained indicating that high coefficient of determination showed that the model can be efficiently be applied to prediction biogas productivity [16].

Figures 1 show the three dimensional (3D) response surface curve of graphical illustration on the effect of pyrolysis temperature and pyrolysis time on the phenol total compound of wood vinegar.
Figure 1. Response surface curve for phenol total compound of wood vinegar showing the interaction between pyrolysis temperature ($X_1$; °C) and times pyrolysis ($X_2$; min)

The maximizing of phenol total compound of wood vinegar was selected as the responses for the combination of independent variables (table 2). The stationer point of phenol total content of wood vinegar, pyrolysis temperature, and pyrolysis times were found to be 420 °C, 122.40 minutes while the maximum of phenol total content of wood vinegar was 3.13%.

The responses of the CCD fitted with a second-order polynomial equation, illustrating the phenol total content, is given by following:

\[ Y = 2.97 + 0.12 X_1 + 0.03 X_2 + 0.23 X_1^2 - 0.24 X_2^2 - 0.24 X_1 X_2 \]

3.2. **Maximizing the acid total content of wood vinegar**

The acid total compounds of wood vinegar from oil palm empty bunches was further optimized using RSM. Two factor levels in coded and un-coded values are shown in table 1. The experimental design and the observed data for acid total content is shown in table 2. The ANOVA was statistically significant (p<0.05) and suggested that at least one of the parameters of the models can explain the experimental variation for acid total content.

Figures 2 shows the three dimensional (3D) response surface curve of graphical illustration on the effect of pyrolysis temperature and pyrolysis time on the acid total compound of wood vinegar.
Figure 2. Response surface curve for acid total compound of wood vinegar showing the interaction between pyrolysis temperature (X₁; °C) and times pyrolysis (X₂; min)

The maximizing of acid total content of wood vinegar was selected as the responses for the combination of independent variables (table 2). The stationary point acid total content of wood vinegar was pyrolysis temperature and pyrolysis times were found to be 422 °C, 118.50 minutes while the maximum acid total content of wood vinegar was 10.04 %.

The responses of the CCD fitted with a second-order polynomial equation, illustrating the acid total content, is given by following:

\[ Y = 9.89 + 0.63 X_1 + 0.70 X_2 - 0.56 X_1^2 + 0.12 X_2^2 - 1.70 X_1 X_2 \]

4. Conclusions
Optimization by RSM-CCD suggested the pyrolysis temperature and pyrolysis time were 420 °C and 122.40 minutes and the maximum phenol total content of wood vinegar was 2.98 %. Meanwhile, the maximum acid total content of wood vinegar was 10.04 % and the pyrolysis temperature and pyrolysis times were 422 °C dan 118.50 minutes.

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