Production of formic acid from oil palm empty fruit bunch via dilute acid hydrolysis by response surface methodology

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Abstract. Formic acid is the simplest carboxylic acid which has myriad applications in food, textiles, agriculture, pharmaceutics, and chemicals. Formic acid can be synthesized from hydrolysis of lignocellulosic biomass. Oil palm empty fruit bunch (OPEFB) is lignocellulosic biomass produced by oil palm industries to which cellulose content has potential for conversion into formic acid by hydrolysis. We investigated effects of three parameters in acid-catalysed hydrolysis reaction of OPEFB such as reaction time (20, 40, 60 minutes), temperature (140, 160, 180 °C), and H2SO4 concentration (0.3; 0.5; 0.7 M) and optimized them to obtain maximum formic acid concentration by using response surface methodology. Microwave assisted alkaline pretreatment of OPEFB sample under microwave radiation at 840 Watt for 9 minutes with 2% NaOH concentration was done prior to hydrolysis. The pretreatment was effective to reduce lignin content of OPEFB from 28.9% to 7.6%. The highest actual formic acid concentration we obtained from the experiment was 2725 ppm at 180 °C, 60 minutes reaction time, and 0.5 M H2SO4. While according to the polynomial model, the optimal condition for obtaining maximum formic acid concentration of 2890.673 ppm was at 180 °C, reaction time of 60 minutes, and 0.3 M H2SO4.

1. Introduction

Indonesia is the world’s largest producer of oil palm where its production is estimated to increase from 38.5 million tons in 2018 to 40.5 million tons in 2019 [1]. The growing palm oil industry sector in Indonesia will also enlarge the availability of palm oil residue. Oil palm empty fruit bunch (OPEFB) is one of the solid wastes from this sector. OPEFB is an example of lignocellulosic biomass which contains 36.67% cellulose, 13.5% hemicellulose, 31.16% lignin, 17.79% extractives, and 0.89% ash [2]. Previous study showed that hemicellulose in OPEFB can be converted into formic acid and levulinic acid while cellulose in OPEFB can be converted into furfural by acid-catalysed hydrolysis reaction [3].

Formic acid (FA) is a valuable chemical product that has myriad current application in agriculture, pharmaceutics, food, textiles, and chemicals due to its strong acidic and reducing properties [4]. FA has also recently been suggested as a promising hydrogen storage component by decomposition to CO2 and H2 with possible reversible FA re-transformation thus it can serve as a platform for chemical energy storage [5]. FA is commonly produced from fossil fuels by the following methods: methyl formate hydrolysis, oxidation of hydrocarbons, hydrolysis of formamide, and preparation of formic acid from formates [6]. Methyl formate hydrolysis is currently dominant covering 90% of the overall installed capacity with 770 kton/year formic acid produced worldwide in 2014 [4]. In recent years, FA can be easily synthesized in laboratory as major by-product of some generation biorefinery process.
such as acid-catalysed hydrolysis reaction. Acid-catalysed hydrolysis reaction of OPEFB had been done in laboratory scale to produce FA with the highest FA concentration obtained of 1427 ppm at reaction temperature of 170 °C for 20 minutes with 1 M H$_2$SO$_4$ as catalyst [7].

This study involved the optimization of some important process parameters of acid-catalysed OPEFB hydrolysis reaction such as reaction time, temperature, and H$_2$SO$_4$ concentration to obtain maximum FA concentration. It is very important to optimize those parameters upon which the yield of FA is dependent to maximize it. The optimization was done by using statistical analysis method called response surface methodology (RSM) which had been applied to study the effect of alkaline pretreatment on the physical properties of OPEFB [8]. RSM based on statistically designed experiments has been found to be very useful in optimizing multivariable processes which is specifically employed for multiple regression analysis of quantitative data obtained from statistically designed experiments [9].

2. Materials and methods

2.1. Materials

OPEFB powder was obtained from Center for Starch Technology (BBTP) Research and Assessment of Technology (BPPT) Lampung, Indonesia. OPEFB was first sieved to get uniform particle size of 30-40 mesh then dried at 105°C for 4 h inside oven. The OPEFB sample was then stored in a closed container at room temperature. Sodium hydroxide pellet for analysis was purchased from Merck. While sulfuric acid 96% was purchased from Mallinckrodt.

2.2. Microwave assisted alkaline pretreatment

Microwave assisted alkaline pretreatment was done using a microwave oven (Electrolux EMS3087X). For pretreatment, 70 g OPEFB sample and 700 mL 2% NaOH solution were mixed well together in 1 L beaker glass. The beaker glass was then sealed tightly with aluminium foil to prevent vapour leakage during pretreatment. Pretreatment was done under 840 Watt microwave power for 9 minutes to obtain maximum delignification. Pretreated OPEFB was then separated from its black liquor by using 10 µm BIPMED BI filter paper and neutralized using distilled hot water at 60 °C. The collected pretreated OPEFB was finally dried inside oven at 80 °C for 12 h and pulverized by using kitchen blender. The pulverized OPEFB sample was stored in sealed plastic bottles at room temperature until used for lignin analysis and acid-catalysed hydrolysis for formic acid production.

2.3. Design of experiment

Response surface methodology (RSM) with Box-Behnken design (BBD) was applied to optimize the process variables influencing formic acid concentration in final liquid fraction from acid-catalysed OPEFB hydrolysis reaction. Three variables were set in this study: reaction time (20, 40, 60 minutes), temperature (140, 160, 180 °C), and H$_2$SO$_4$ concentration (0.3; 0.5; 0.7 M) as shown in Table 1. The hydrolysis reaction was done in a laboratory scale autoclave reactor. For each experiment, 10 gr OPEFB and 250 mL sulfuric acid solution were mixed well and reacted under 150 rpm agitation in the reactor. The liquid fraction from each experiment was then filtered by membrane filter to separate unused solid hydrolysate and finally stored in a tightly-closed dark glass container under refrigerated condition for further analysis. The experimental design consisted of total fifteen experimental runs and software Design Expert v.11 (Stat Ease Inc., Minneapolis, MN, USA) was employed to perform analysis of variance (ANOVA), to optimize the process variables, and to generate response surface curves.

| Table 1. Factors and their levels as used in the Box-Behnken model design of OPEFB hydrolysis. |
Factors

| Coded Parameters | Uncoded Parameters  | Unit     | Levels |
|------------------|---------------------|----------|--------|
| A                | Reaction time       | Minute   | -1     |
| B                | Temperature         | °C       | 0      |
| C                | Acid concentration  | Molar    | +1     |

2.4. Analysis methods

Lignin contents of raw and pretreated OPEFB were analysed according to TAPPI T-222 om-83. Briefly, OPEFB was hydrolysed and solubilized by H$_2$SO$_4$. The acid-insoluble lignin was filtered off, dried and weighed. In this test method, lignin is defined as wood or pulp constituent insoluble in 72% H$_2$SO$_4$[10]. Formic acid concentration was analysed by using HPLC equipped with HPX – 87H ion exclusion column and refractive index detector at 60 °C. Sulfuric acid 0.006 N solution was used as mobile phase with 1 mL/min flow rate.

3. Results and discussion

Microwave assisted alkaline pretreatment of OPEFB at 840 Watt for 9 minutes with 2% NaOH could reduce the lignin content of OPEFB from 28.9% to 7.6% or equals to 73.3% lignin removal. In this process, lignin was removed to disrupt the lignocellulose structure of OPEFB so that hemicellulose could be effectively converted into FA by acid catalyst.

The results at each point based on experimental Box-Behnken design template are presented in Table 2. The highest FA concentration of 2725 ppm was achieved at hydrolysis conditions of 60 minutes reaction time, 180 °C temperature, and 0.5 M acid concentration. This result is higher than previous research by Panjaitan (2017) whose highest FA concentration was only 1427 ppm at reaction temperature of 170 °C for 20 minutes with 1 M H$_2$SO$_4$ as catalyst [7]. Some experiments in this research could not detect formic acid possibly because the reaction conditions were more favourable for furfural conversion from hemicellulose than formic acid production from cellulose.

From Table 3 it is showed that the model is statistically significant with p-value at 95% confident level due to higher F-value (55.66) than p-value (0.0002). The significance of each regression coefficient and the interactions between the hydrolysis variables was evaluated using p-value. In this model, both variable A (reaction time) and B (reaction temperature) are significant. While variable C (acid concentration) is not significant. Moreover, the interactive effects between variables AB and quadratic effect of variables B$^2$ shows significant effects on OPEFB hydrolysis for FA production.

The second-degree polynomial model for OPEFB hydrolysis generated from Design Expert software in terms of coded equation is given by Eqs. (1) where A, B, and C are reaction time, temperature, and acid concentration respectively. From this equation, both reaction time and temperature have positive effect on FA concentration obtained while acid concentration has negative effect on it. That means increasing reaction time and/or temperature will give more FA concentration while increasing acid concentration will decrease FA concentration obtained. Reaction temperature has higher positive effect than reaction time. Significant temperature effect can be related with low activation energy of furfural degradation into levulinic acid and FA which is only 9.89 kJ/mole and moderate activation energy of 5-hydroxymethylfurfural (HMF) conversion into levulinic acid and FA [3]. According to the polynomial model, the optimal condition for obtaining maximum FA concentration of 2890.673 ppm is as follows: reaction time of 60 minutes, temperature of 180 °C, and acid concentration of 0.3 M.

$$\text{Formic acid concentration (ppm)} = 422.12A + 839.25B - 51.88C + 424.75AB - 4.50AC - 99.25BC + 308.25A^2 + 629.50B^2 + 111.25C^2$$  \hspace{1cm} (1)

Figure 1 shows 3D RSM curves generated from Design Expert v.11 for OPEFB hydrolysis in this study. It can be seen that highest FA concentration can be obtained at highest temperature and reaction
time, highest reaction time and lowest acid concentration, and highest temperature and lowest acid concentration. From Figure 1, decreasing the temperature and reaction time tends to decrease FA production significantly. While decreasing the acid concentration tends to increase FA production not significantly.

Table 2. Box-Behnken model in uncoded forms of process variables and values of experimental data for OPEFB hydrolysis.

| Run | Reaction Time (min) | Temperature (°C) | Acid Concentration (M) | Formic Acid Concentration (ppm) |
|-----|---------------------|------------------|------------------------|---------------------------------|
| A   |                     |                  |                        |                                 |
| 1   | 40                  | 140              | 0.3                    | nd                              |
| 2   | 40                  | 180              | 0.7                    | 1283                            |
| 3   | 60                  | 180              | 0.5                    | 2725                            |
| 4   | 60                  | 140              | 0.5                    | nd                              |
| 5   | 40                  | 160              | 0.5                    | nd                              |
| 6   | 60                  | 160              | 0.7                    | 830                             |
| 7   | 40                  | 160              | 0.5                    | nd                              |
| 8   | 20                  | 180              | 0.5                    | 1026                            |
| 9   | 40                  | 160              | 0.5                    | nd                              |
| 10  | 40                  | 140              | 0.7                    | nd                              |
| 11  | 20                  | 160              | 0.3                    | nd                              |
| 12  | 20                  | 160              | 0.7                    | nd                              |
| 13  | 40                  | 180              | 0.3                    | 1680                            |
| 14  | 20                  | 140              | 0.5                    | nd                              |
| 15  | 60                  | 160              | 0.3                    | 848                             |

nd = not detected

Table 3. Statistical analysis for computed OPEFB hydrolysis.

| Source        | Sum of Squares | df | Mean Square | F-value | p-value |
|---------------|----------------|----|-------------|---------|---------|
| Model         | 9.564E+06      | 9  | 1.063E+06   | 55.56   | 0.0002  |
| A-Time        | 1.426E+06      | 1  | 1.426E+06   | 74.53   | 0.0003  |
| B-Temp.       | 5.635E+06      | 1  | 5.635E+06   | 294.62  | 0.0001  |
| C-Conc.       | 21528.13       | 1  | 21528.13    | 1.13    | 0.3372  |
| AB            | 7.217E+05      | 1  | 7.217E+05   | 37.73   | 0.0017  |
| AC            | 81.00          | 1  | 81.00       | 0.0042  | 0.9506  |
| BC            | 39402.25       | 1  | 39402.25    | 2.06    | 0.2107  |
| A²            | 3.508E+05      | 1  | 3.508E+05   | 18.34   | 0.0078  |
| B²            | 1.463E+06      | 1  | 1.463E+06   | 76.50   | 0.0003  |
| C²            | 45698.08       | 1  | 45698.08    | 2.39    | 0.1828  |
| Residual      | 95628.25       | 5  | 19125.65    |         |         |
| Lack of Fit   | 95628.25       | 3  | 31876.08    |         |         |
| Pure Error    | 0.0000         | 2  | 0.0000      |         |         |
| Cor Total     | 9.660E+06      | 14 |             |         |         |

Other statistical parameter

| Std. Dev. | Mean | C.V. % | PRESS | R² | Adjusted R² | Predicted R² | Adeq Precision |
|-----------|------|--------|-------|----|-------------|--------------|----------------|
| 138.30    | 559.47 | 24.72  | 1.530E+06 | 0.9901 | 0.9723     | 0.8416      | 24.5289        |
Figure 1. RSM 3D curves for acid-catalysed OPEFB hydrolysis reaction.
4. Conclusion
In this study, we investigated formic acid production from acid-catalysed hydrolysis reaction of OPEFB and optimized it by using response surface methodology. The highest actual formic acid concentration we obtained from the experiment was 2725 ppm at 180 °C, 60 minutes reaction time, and 0.5 M H₂SO₄. While according to the polynomial model, the optimal condition for obtaining maximum formic acid concentration of 2890.673 ppm was at 180 °C, reaction time of 60 minutes, and 0.3 M H₂SO₄.

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References
[1] Mcdonald G and Rahmanulloh A 2018 Indonesia Oilseeds and Products Annual 2018 (Jakarta: USDA Foreign Agricultural Service)
[2] Isroi, Cifriadi A, Panji T, Wibowo N A and Syamsu K 2017 IOP Conf. Ser.: Earth Environ. Sci. 65 012011
[3] Gozan M, Panjaitan J R H, Tristantini D, Alamsyah R and Yoo Y J 2018 Int. J. Chem. Eng. 2018 1-12
[4] Rumayor M, Dominguez-Ramos A and Irabien A 2018 Appl. Sci. 8 914
[5] Grasemann M and Laurenczy G 2012 Energ. Environ. Sci. 5 8171-81
[6] Hietala J, Vuori A, Johnsson P, Pollari I, Reutemann W and Kieczka H 2000 Ullmann’s Encyclopedia of Industrial Chemistry (Weinheim; Wiley-VCH Verlag GmbH & Co.)
[7] Panjaitan J R H and Gozan M 2017 Int. J. Appl. Eng. Res. 12 4382-90
[8] Fatra W, Rouhillahi H, Helwani Z, Zulfansyah Z and Asmura J 2016 Int. J. Technol. 7 1026-34
[9] Montgomery D C 2005 Design and Analysis of Experiment 6th Edition (New York: John Wiley and Sons Inc.)
[10] Piarpuzán D, Quintero J A and Cardona C A 2011 Biomass. Bioenerg. 35 1130-37