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The use of fractional factorial design to analyze the effect of sulfuric acid concentration and temperature on furfural yield

Said Zul Amraini [a], Rozanna Sri Irianty [a], Nirwana Hamzah [a], Sri Rezeki Muria [a], Novia Liana Sari [a], Rachmad Aidil Azhar [a], Reno Susanto [b]

[a] *Departement of Chemical Engineering, Faculty of Engineering, University of Riau, Pekanbaru 28293, Indonesia*
[b] *Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung 40135, Indonesia*

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ABSTRACT

Furfural is a compound derived from monosaccharides that has wide application in several industries and can also be synthesized into its derivatives, such as furfuryl alcohol and furan. Furfural production uses materials containing lignocellulose, such as empty fruit bunch (EFB), with an acid chemical treatment to break the lignocellulosic bonds so that furfural is obtained. Making furfural begins with reducing the size of the EFB and drying it until the moisture content is below 10%. This study used a fractional factorial design with a variation of sulfuric acid concentration of 6–10% (v/v) and temperature variations of 110–130 ℃ for 60 min. During the process, furfural goes through two reaction stages, namely hydrolysis and dehydration, with the help of a sulfuric acid catalyst, where the hydrolysis reaction will form pentoses. Then, pentoses are converted into furfural by the elimination of water as a dehydration reaction process. Furfural products are separated by extraction and distillation. Based on the results of the FTIR analysis, the furfural constituent groups are aromatic, ether, and aldehyde groups. The results of this study indicate that the variables that have a significant effect on furfural density and yield are concentration and temperature, with the highest furfural yield obtained at 10% sulfuric acid concentration at a temperature of 130 ℃, which is 7.31% with a density of 1.1596 g/mL.

1. Introduction

Furfural is a compound derived from monosaccharides that has wide application in several industries and can also be synthesized into its derivatives, such as furfuryl alcohol and furan. Domestic furfural is currently used in two parts, namely the lubricating oil industry at 82% and other consumptions at 18%, which is mainly consumed by synthetic rubber. Several studies have investigated the yield of furfural from different feedstocks, such as corn stover, sugarcane bagasse, and wheat straw, and have reported varying results [1,2]. In recent years, attention has turned to the use of oil palm empty fruit bunches (EFB) as a potential feedstock for furfural production due to their abundant availability and low cost. Based on data from the Directorate General of Plantations, the estimated area of oil palm plantations in Riau Province in 2021 is 2,895,003 ha, with a production capacity of 10,270,149 tons [3].

Empty Palm Oil Bunches (EFB) contain lignocellulose, consisting of cellulose, hemicellulose, and lignin, which are linked together, but the solid waste of EFB has yet to be utilized optimally. One of the efforts to use alternative EFB is as a raw material for making furfural. Furfural is used in several industries, such as oil processing, plastics, resin manufacture, cosmetics, and pharmaceuticals [4]. The efficient conversion of various biomass sources to bioethanol relies on a pre-treatment process to reduce cell wall recalcitrance and enable a higher hydrolysis yield [5]. The firmness of the pre-treatment is determined by several factors, the most relevant of which are reactant concentration, temperature, time, pressure, solid–liquid ratio, and the presence of a catalyst [6]. To optimize the furfural yield from EFB, it is essential to identify the key factors that influence the reaction and understand their effects.

In this study, furfural was produced from EFB using dilute acid. We focus on two key factors that influence the density and yield of furfural from EFB: the acid concentration and the temperature. We aim to investigate the effects of these two factors on lignocellulose content and analyzed the furfural density and yield using full fac-

E-mail address: saidzulamraini@eng.unri.ac.id (S.Z. Amraini)

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torial 2^3 analysis and developed an empirical model that describes the effect of various variables in this study.

2. Methods

2.1. Raw material

The raw material for empty fruit bunches (EFB) collected from a local palm oil mill (PTPN V Sungai Pagar) was chopped to a size of 0.5–2 cm and dried under the sun until the moisture content was below 10%.

2.2. Acid hydrolysis

Acid hydrolysis was carried out in a 1000 mL Erlenmeyer flask. 15 g of EFB was mixed with various concentrations of 150 mL of sulfuric acid (H_2SO_4: 6–10% v/v) solutions (Merck, Germany) at the operating temperatures of 110–130 ℃ for 1 h and with the solid: liquid ratio of 1:10. After that, the solids were filtered and washed with distilled water. The solution resulting from the hydrolysis process (black liquor) was added with chloroform (Merck, Germany) with purity 98% to extract furfural allowed to stand for 48 h. After deposition, three layers were determined: the chloroform and product layers at the bottom, lignin in the middle, and the water layer at the top. The chloroform solution and the product were added with 0,5 g Na_2SO_4 (Merck, Germany) to remove water. The product was separated from chloroform by distillation at 63℃. The process flow diagram can be seen in Fig. 1.

2.3. Characterizations

In this manuscript, few characterizations were conducted for instance lignocellulose content was analyzed gravimetrically based on the previous method [7], density of the furfural sample (Eq. (1)), furfural yield [17] (Eq. (2)) and the functional groups determinations.

$$\rho = \frac{m2 - m1}{V} \tag{1}$$

where,

m1: Mass of empty pycnometer (grams)
m2: The mass of the pycnometer contains furfural (grams)
V1: Pycnometer volume (mL)

$$Yield = \frac{\frac{m}{n}\, x\, (V_2 - V_1)\, x\, N}{\text{Mass of EFB (mg)}}\, x\, 100\% \tag{2}$$

where,

m: Overall reaction volume (mL)
n: Sample volume (mL)
V_1: Volume of $Na_2S_2O_3$ sample titration (mL)
V_2: Volume of $Na_2S_2O_3$ titration blank (mL)
N: Normality $Na_2S_2O_3$

Functional groups of the chemical compounds were determined using the analysis from Fourier Transform.

Infrared Spectroscopy (FTIR) measurement (Shimadzu IR, Europa GmbH) using ASTM E 1235.

2.4. Statistical analysis

The data were fully factorial analyzed using Minitab (v.20, Minitab, Inc) (licensed from Institut Teknologi Bandung) to determine the variables that affect furfural density and yield and to develop an empirical model that describes the effect of various variables that affect the density and yield of furfural with 3 repetition on center point (the same results of yield of furfural and furfural density were inputted to the ANOVA. ANOVA was applied to detect statistically significant changes in furfural yield with a 95% level of confidence ($p < 0.05$). The full factorial design of 2^2 design can be seen in Table 1.

A full factorial central composite design is used to acquire data to fit an empirical quadratic model, which has the following form in the case of two screened factors (Eq. 3):

$$Y = b_0 + A_1 + B_2 + A_1B_2 + Ct\ Pt \tag{3}$$

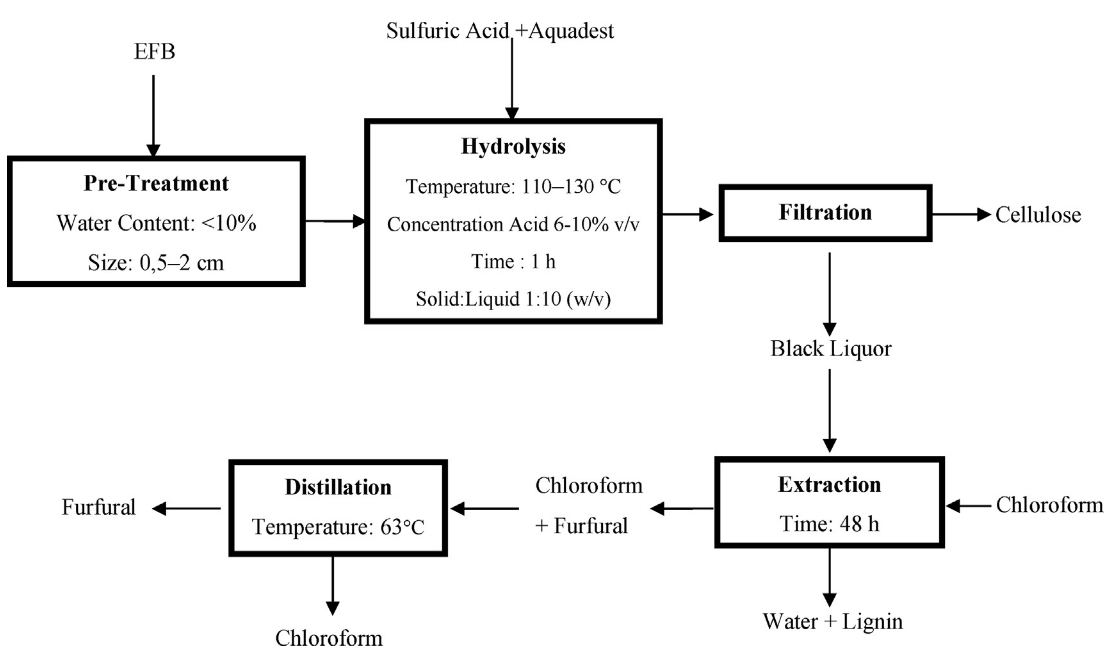

Fig. 1. Block Flow Diagram Furfural Production from EFB.

Table 1
Factor levels evaluated in a fractional factorial design.

Variable	Low Level (-1)	Center Point (0)	High Level (+1)
Sulfuric Acid Concentration (%)	6	8	10
Temperature (℃)	110	120	130

Where the screened factors are A_1 and B_2. Y, b_0 and Ct Pt stand for response, intercept, and center point respectively. This design considers three replicates at the center points and two independent variables with two levels. So it needs seven experiments for this procedure.

3. Results and discussion

3.1. Chemical composition of EFB

Figs. 2 and 3 show the chemical composition of the EFB used in this study. The best hemicellulose content was obtained at a concentration of 10% sulfuric acid and a temperature of 130 ℃, which was 30%. Figs. 2 and 3 show that the acid catalyst can break down lignocellulose components into cellulose, hemicellulose, and lignin components. The results of these data indicate that the concentration of catalyst and reaction temperature can increase the percentage of chemical composition, especially hemicellulose, in the composition of furfural manufacture [8].

3.2. Furfural characterization

3.2.1. Furfural density

The results of the density in this study can be seen in Fig. 4. Theoretically, the density range of furfural is between 1.149 and 1.160 g/mL [9,10]. Fig. 4 shows that the only variation in the range of 10% H_2SO_4 concentration at the highest temperature of 130 ℃ is 1.1596 g/mL. At the same time, the research conducted by Kurniasih et al. [11] obtained a furfural density of 1.3409 g/mL. The density increases with the increased concentration of furfural [12].

3.2.2. Furfural identification via FTIR analysis

The FTIR test aims to find information related to the chemical bonds contained in furfural. The furfural used in the FTIR analysis is the best furfural with the highest furfural yield at a concentration of 10% sulfuric acid with a temperature of 130 ℃ at 7.31%. The IR spectra of the empty fruit bunches furfural produced to show the presence of furfural constituent groups, namely aromatic, ether, and aldehyde groups. The following is research data with literature from the Fourier Transformed Infrared (FTIR) Furfural test results in Table 2, which can be seen in Fig. 5.

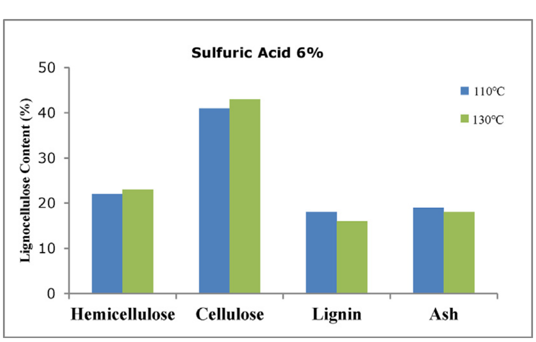

Fig. 2. Effect of temperature and sulfuric acid (6% v/v) on lignocellulose content.

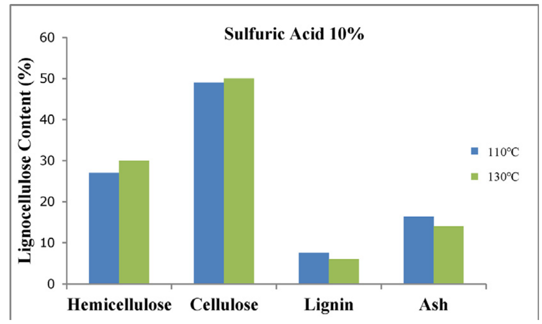

Fig. 3. Effect of temperature and sulfuric acid (10% v/v) on lignocellulose content.

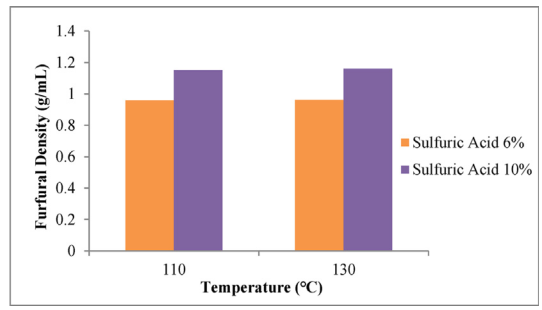

Fig. 4. Furfural Density Analysis Results Data.

Table 2
FTIR analysis result.

Group	Literature Silverstein et al. [13]	This Study	Kurniasih et al., [11]
C–H (aromatic)	3003–3077	3013.90	3133.30
C–H (aldehyde)	2695–2830	2733.25	2848/63
C = O (aldehyde)	1720–1740	1722.51	1667
C–O–C (ether)	1200–1275	1216.17	1276.60
C = C (aromatic)	1400–1500 and 1585–1600	1446.67	1567/36

Based on Fig. 5, the results of the furfural FTIR analysis carried out in this study indicate from the infrared spectrum above that the presence of furfural constituent groups is supported by the presence of C–H (aromatic) and C–H (aldehyde) vibrational peaks in the 3013.90 cm^{-1} and 2733.25 cm^{-1} absorption region. The presence of C = O (aldehyde) bonds in the 1722.51 cm^{-1} region, C = C (aromatic) in the 1446.67 cm^{-1} absorption region, and C–O–C (eter) in the 1216.17 cm^{-1} absorption region. Table 2 shows that, theoretically, the results of the furfural FTIR analysis carried out by this study are in the wavelength range for the furfural constituent groups. From Fig. 5, it can be concluded that the study results follow the results of the furfural FTIR analysis conducted by Kurniasih et al. [11]. The results of this study are also in agreement with the research conducted by Mitarlis et al. [14]. The following absorptions indicated the clusters: stretching C–C (aromatic) in the absorption area of 3132.8 cm^{-1}; C–H (aldehyde) in the absorption area of 2855 cm^{-1}; C = O (aldehyde) in the absorption region of 1683.9 cm^{-1}; C = C (aromatic) in the absorption area of 1567.4 cm^{-1}; and C-O-C () in the absorption area of 1154.1 cm^{-1}.

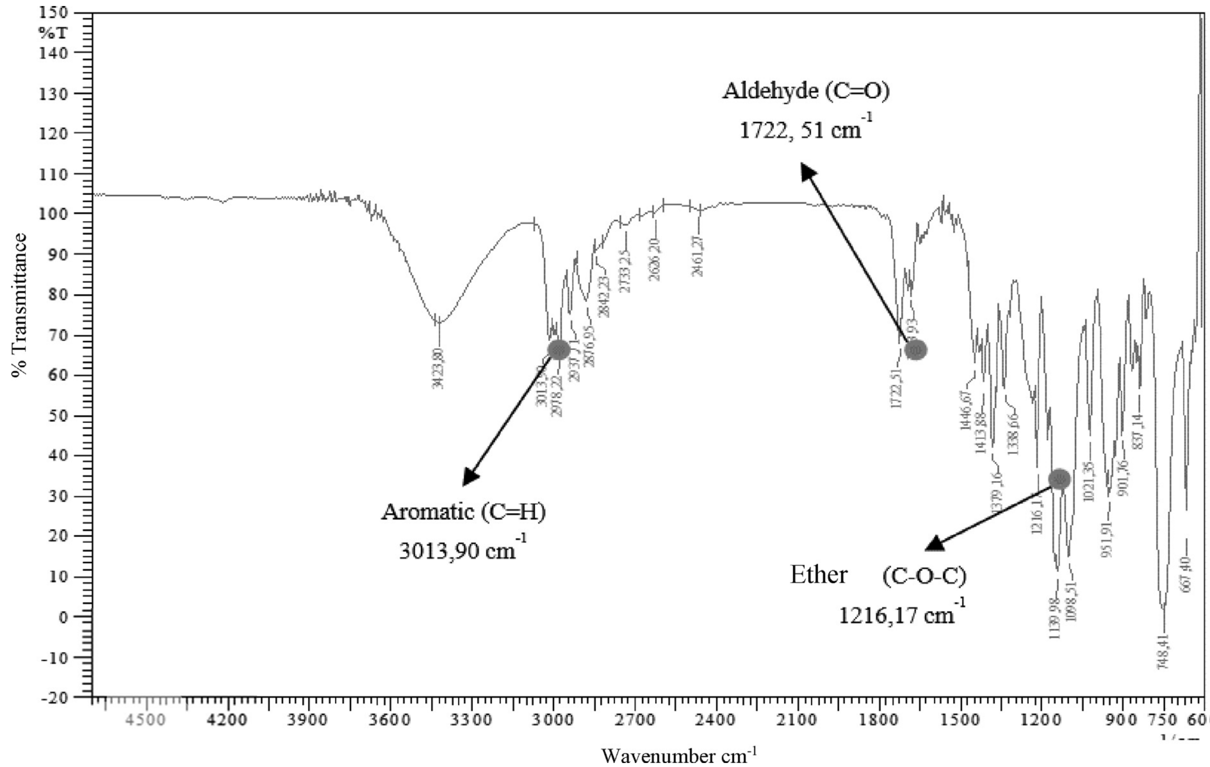

Fig. 5. FTIR Furfural.

3.3. Effect of temperature and acid concentration on furfural yield

In this study, as seen in Fig. 6, the furfural yield is determined by the variation of its concentration 6–10% (v/v), and the reaction temperature is 110–130 ℃. Overall, furfural yield was in the range of 5.96–7.31%. Based on Fig. 6, the 10% concentration of H_2SO_4 solvent at a temperature of 130 ℃ resulted in the highest furfural yield of 7.31%. The lowest furfural yield of 5.96% was obtained at 110 ℃ with a 6% (v/v) sulfuric acid addition. This study obtained the highest furfural yield when compared to the study of Kusyanto & Rachmadina [15], which obtained a furfural yield of 0.962% at 9% H_2SO_4 concentration at a temperature of 90 ℃ for 75 min. This is in accordance with the theory that pentoses will release water molecules in hot and acidic conditions to form furfural, so the amount of furfural obtained is strongly influenced by the amount of pentose formed. Therefore, the greater the pentose sugar formed, the greater the furfural obtained [16]. In the study of Hambali et al. [17] using rice husks, the furfural yield was 1.87% with H_2SO_4 at 2%, 100 ℃, 2 Hours and Mardina et al. [18] 5.441% with H_2SO_4 operating conditions (2)%, 100 ℃. According to Setyadji [8], the reaction rate of furfural formation will be faster in the presence of sulfuric acid because sulfuric acid acts as a catalyst that lowers the activation energy of the reaction.

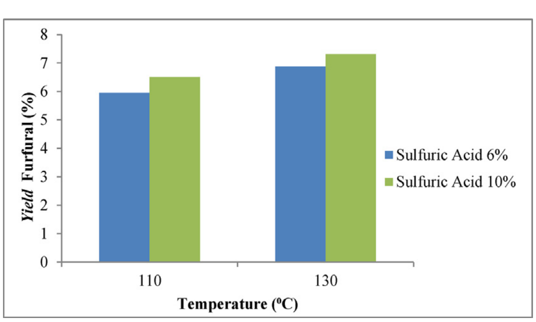

Fig. 6. Temperature and acid concentration vs furfural yield.

According to Dwijanarko & Mulyadi [19], the increase in furfural obtained was caused by the increasing concentration of sulfuric acid to accelerate the conversion process of water molecules on hydrolysis, resulting in the water content in the cooking liquid (solvent) decreasing during hydrolysis, and this situation would increase the amount of sugar produced. In addition, it can be seen that temperature also affects the increase in yield at each variation of H_2SO_4 concentration. According to Setyadji [8], in general, with the use of acid solvents, the higher the reaction temperature, the greater the yield of furfural produced. However, when the hydrolysis temperature increases, it can cause degradation into other organic compounds. However, higher acid dosages beyond 0.5 wt % reduced furfural yield due to the dominance of furfural degradation reactions [20,21]. The resulting solution indicates degradation, which forms a black resin precipitate [19].

3.4. Fractional factorial design analysis

Two-level factorial design is widely used in the presence of several factors with possible interactions. The experiment aims to

Table 3
Fractional factorial experimental furfural design result.

Concentration (%)	Temp (℃)	Yield (%)	Density(g/mL)
6	130	6.88	0.961
6	110	5.96	0.959
10	130	7.31	1.159
10	110	6.50	1.150
8	120	6.70	1.079
8	120	6.70	1.079
8	120	6.70	1.079

Table 4
ANOVA concentration and temperature vs density.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	3	0.038671	0.012890	3156.85	0.000
Linear	2	0.037861	0.018930	4635.98	0.000
Concentration	1	0.037830	0.037830	9264.55	0.000
Temperature	1	0.000030	0.000030	7.41	0.072
Curvature	1	0.000811	0.000811	198.60	0.001
Error	3	0.000012	0.000004		
Lack-of-Fit	1	0.000012	0.000012	*	*
Pure Error	2	0.000000	0.000000		
Total	6	0.038684			

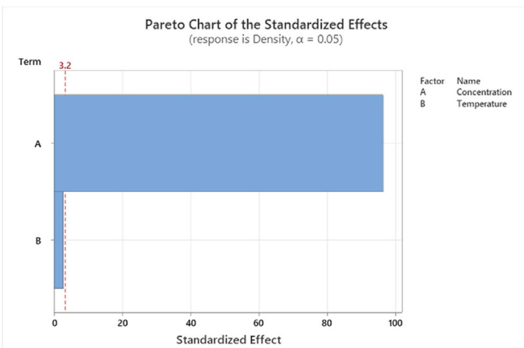

Fig. 7. Pareto chart concentration and temperature vs density.

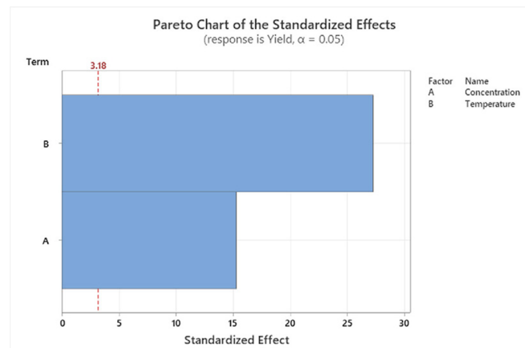

Fig. 8. Pareto chart concentration and temperature vs yield.

obtain a good furfural yield and density by applying a full factorial design of 2^2. The number of runs carried out was 4, with 3 replicas at the center point. The results of the full factorial design of 2^2 can be seen in Table 3.

3.4.1. ANOVA analysis based on furfural density as response

Based on the ANOVA results in Table 4 and Fig. 7, it is found that the variables that affect the density are concentration (A), which have a P-Value < 0.05. Variable temperature (B) and interaction of the AB variables did not affect the furfural density. The regression equation obtained from the downsizing model has an R-squared of 99.97% and an R-squared (adj) of 99.94%, which can be seen in equation (1) (uncoded).

$$\text{Density} = 0.6352 + 0.048625\ \text{Concentration} + 0.000275\ \text{Temperature} + 0.02175\ Ct\ Pt \tag{3}$$

3.4.2. ANOVA analysis based on furfural yield as response

Based on the ANOVA results in Table 5 and Fig. 8, it is found that the variables that affect the yield are concentration (A) and temperature (B) which have a P-value of < 0.05 and shown as the effects are greater than the outlier line (red dotted line) as shown as in Fig. 8. The interaction of the AB variables did not significantly affect the furfural yield. The interaction of the AB variables did not affect the furfural density. The regression equation obtained from the downsizing model has an R-squared of 99.69% and an R-squared (adj) of 99.39% which can be seen in equation (2) (uncoded)

$$\text{Yield} = 0.503 + 0.12125\ \text{Concentration} + 0.04325\ \text{Temperature} + 0,0375\ \text{Ct Pt} \tag{4}$$

4. Conclusion

In this study, furfural production using EFB obtained the highest yield of 7.31% with a concentration of 10% sulfuric acid and a hydrolysis temperature of 130 ℃ with a density of 1.1596 g/mL, which was in accordance with the standard. Furfural production is influenced by the hemicellulose content of the EFB used. The variables that significantly affect density of furfural in this study is concentration (A) and for the yield are concentration (A) and temperature (B). These results concluded that EFB could be a potential raw material and sulfuric acid pre-treatment could be a

Table 5
ANOVA concentration and temperature vs. yield.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	3	0.985861	0.328620	325.90	0.000
Linear	2	0.983450	0.491725	487.66	0.000
Concentration	1	0.235225	0.235225	233.28	0.001
Temperature	1	0.748225	0.748225	742.04	0.000
Curvature	1	0.002411	0.002411	2.39	0.220
Error	3	0.003025	0.001008		
Lack-of-Fit	1	0.003025	0.003025	*	*
Pure Error	2	0.000000	0.000000		
Total	6	0.988886			

common initial process in a biorefinery to produce cellulose, furfural, and lignin.

CRediT authorship contribution statement

Said Zul Amraini: Conceptualization, Methodology, Resources. **Rozanna Sri Irianty:** Writing – review & editing. **Nirwana:** Writing – review & editing. **Sri Rezeki Muria:** Supervision. **Novia Liana Sari:** Visualization, Investigation, Writing – original draft. **Rachmad Aidil Azhar:** Visualization, Investigation, Writing – original draft. **Reno Susanto:** Data curation, Software, Validation.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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