Abstract The productions of levulinic acid from corncob were carried out by subcritical water process in a temperature range of 180–220 °C, reaction time of 30, 45, and 60 min. The acid modified zeolite was used as the catalyst in the subcritical water process. The ratio between the mass of zeolite and volume of hydrochloric acid in the modification process were 1:5, 1:10 and 1:15. The optimum values of the process variables in the subcritical water process for the production of levulinic acid from corncob were: Temperature of 200 °C; 1:15 zeolite to acid ratio; and reaction time of 60 min. The maximum levulinic acid concentration obtained in this study was 52,480 ppm or 262.4 mg/g dried corncob.

Keywords Levulinic acid · Subcritical water · Modified zeolite

Introduction

Levulinic acid (4-oxopentanoic acid or γ-ketovaleric acid) is an organic compound with a short-chain fatty acids containing carbonyl group of ketones and carboxylic acids. Levulinic acid is an important chemical platform for the production of various organic compounds. It can be used for the production of polymers, resins, fuel additives, flavors, and others high-added organic substances. This chemical can be produced through several routes [1–7] and one of the most promising processes is the dehydrative treatment of biomass or carbohydrate with various kinds of acids.

Biomass can be used as the precursor to produce levulinic acid and other organic chemicals. The use of biomass as the raw material for the production of levulinic acid in commercial scale was developed by Biofine renewables [3, 7]. The Biofine process consists of two different stages of processes, the first stage of the process is the production of 5-hydroxymethylfurfural (HMF) while the second stage is the production of levulinic acid [3].

Several studies have reported that various types of homogeneous as well as heterogeneous catalysts have been used for the preparation of levulinic acid from lignocellulosic biomass [2–4, 7–9]. Usually, the homogeneous catalysts are more effective than some of heterogeneous catalysts; however, the drawbacks of the use of homogeneous catalysts for levulinic acid production are associated with the corrosion of the equipment, environmental problem, and re-use of the catalyst. One of the advantages of using heterogeneous catalyst for the production of levulinic acid is the heterogeneous catalyst can be easily recovered and reused [3].

Zeolites have been used as catalysts or catalyst supports in many reaction systems. The properties of zeolites, such
as porosity, types and the amount of surface acidity, and the type of the structure greatly influence the selectivity and catalytic performance of these materials. A number of synthetic zeolites have been used as the catalyst for the levulinic acid production, however, zeolites with low acidity and porosity gave a poor catalytic performance on the conversion of sugars into levulinic acid [3]. Zeolite-type materials, such as faujasite and modernite, have been used for the synthesis of levulinic acid from C₆ sugars and cellulose [6, 8, 10, 11].

Some of agricultural wastes and other lignocellulosic materials have the potential application as the precursors for levulinic acid production [12]. The production of levulinic acid from agricultural waste materials involves two critical steps of processes; the first process is hydrolysis, in the hydrolysis process the hemicellulose and cellulose are converted into C₅ and C₆ sugars. The second process is dehydration process, in this process the C₅ and C₆ sugars are dehydrated into levulinic acid and furan derivatives [12].

In this study, the production of levulinic acid from corncob was conducted on subcritical water condition using acid modified zeolite as heterogeneous catalyst. Subcritical water (SCW) process is an environmentally friendly method, which can be applied in various applications, such as extraction, hydrolysis, and wet oxidation of organic compounds. Subcritical water is defined as the hot compressed water (HCW) or hydrothermal liquefaction at a temperature between 100 and 374 °C under conditions of high pressure to maintain water in the liquid form [13]. At this subcritical condition, water acts as solvent and catalyst for the hydrolysis of cellulose and hemicellulose in the corncob. The use of acid modified zeolite increases the acidity of the system leading to the increase of the hydrolysis and dehydration rate of reactions and subsequently increases the yield of levulinic acid.

To the best of our knowledge, there is no single study used the subcritical water process combined with acid modified zeolite as the catalyst in the production of levulinic acid from lignocellulosic waste material (corncob). The optimum condition for the production of levulinic acid from corncob was determined by Response Surface Methodology (RSM).

**Experimental**

**Materials**

Corncoaks used in this study were obtained from a local market in Surabaya, East Java, Indonesia. Prior to use, the corncobs were repeatedly washed with tap water to remove dirt. Subsequently the corncobs were dried in an oven (Memmert, type VM.2500) at 110 °C for 4 h. The dried corncobs were pulverized into powder (20/60 mesh) using a JUNKE & KUNKEL hammer mill. The ultimate analysis of the corncob was determined using a CHNS/O analyzer model 2400 from Perkin-Elmer, while the proximate analysis was conducted according to the procedure of ASTM. The results of ultimate and proximate analyses of the corncob are summarized in Table 1.

Natural zeolite used in this research was obtained from Ponorogo, East Java, Indonesia. The purification of natural zeolite was conducted using hydrogen peroxide solution (H₂O₂) at room temperature (30 °C) to remove organic impurities. The purified zeolite then was pulverized to particle size of 40/60 mesh. The chemical composition of the purified natural zeolite was SiO₂ (60.14 %), Al₂O₃ (12.52 %), CaO (2.51 %), Fe₂O₃ (2.49 %), Na₂O (2.44 %), K₂O (1.28 %), MgO (0.49 %), H₂O (14.40 %), and loss on ignition (3.73 %).

All chemicals used in this study, such as sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrogen peroxide (H₂O₂), the standard reference of levulinic acid, etc., were purchased from Sigma Aldrich Singapore and directly used without any further purification.

**Natural zeolite modification**

The natural zeolite was modified using hydrochloric acid solution (2 N). The ratio between the zeolite powder and hydrochloric acid were 1:5, 1:10, and 1:15 (weight/volume). Thirty grams of zeolite powder were mixed with a certain volume of HCl solution and transferred into a round bottom flask. Subsequently the mixture was heated at 70 °C under reflux and continuous stirring at 500 rpm for 24 h. After the modification completed, the acid modified zeolite was separated from the mixture by vacuum filtration system. The solid was repeatedly washed with distilled water.

| Component | Corncob, wt% | NaOH pretreated corncob, wt% |
|-----------|-------------|----------------------------|
| Carbon    | 54.1        | 53.8                       |
| Hydrogen  | 6.8         | 6.9                        |
| Nitrogen  | 0.3         | 0.2                        |
| Sulfur    | 0.1         | 0.1                        |
| Oxygen    | 38.7        | 39.0                       |

Table 1 Proximate and ultimate analysis of corncob and its pretreated form
water to remove the excess HCl solution. The acid modified zeolite was dried in oven at 110 °C for 24 h to remove free moisture content. Then, modified zeolite was calcined in a furnace at a temperature of 400 °C for 4 h.

**Delignification process**

Delignification process was carried out by soaking of corncob powder into 20 % of NaOH solution. The ratio between solid and solution was 1:10 (weight/volume). The delignification process was conducted at a temperature of 30 °C under constant stirring (500 rpm). After the process completed (24 h), the treated corncob was separated from the liquid using vacuum filtration system. The biomass was repeatedly washed with distilled water until the pH of the washing solution around 6.5–7. Subsequently the treated corncob was dried at 110 °C for 24 h.

**Conversion of corncob to levulinic acid**

The preparation of levulinic acid from corncob was conducted in a subcritical reactor system. The subcritical reactor system consists of 150 ml high pressure stainless steel vessel, a pressure gage, an external electrical heating system, type K thermocouple, and M8 screws for tightening. The reactor system was fitted in a subcritical reactor system. The subcritical condition was achieved, the remaining n-butylamine in the solution was determined by titration using 0.016 M trichloroacetic acid solution in benzene, and 2,4 dinitrophenol was used as the indicator.

**HPLC analysis**

The organic compounds in the aqueous phase of the product from subcritical water process was analyzed using a Jasco chromatographic separation module consisting of a model PU-2089 quaternary low pressure gradient pump, a model RI-2031 refractive index detector and a model LC-NetII/ADC hardware interface system. Prior to the injection in the HPLC system, all of the liquid samples were filtered through a 0.22 μm PVDF syringe filter. The analysis of monomeric sugars was conducted with an Aminex HPX-87P sugar column (Bio-Rad, 300 × 7.8 mm) using degassed HPLC-grade water isocratically flowing at a rate of 0.60 ml/min. The column was operated at 85 °C. For the analysis of organic compounds, a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) was used as the separating column. The isocratic elution of sulfuric acid aqueous solution (5 mM) was used as the mobile phase with the flow rate of 0.6 ml/min. The column oven was set at 55 °C. Details of the procedure can be seen elsewhere [12].
Results and discussion

To determine the chemical composition of corn cob and sodium hydroxide treated corn cob, the thermal gravimetric Analysis (TGA) was conducted under the nitrogen environment. The TGA curves of both samples are given in Fig. 1. At temperature between 50 and 200 °C, the weight loss of corn cob and the pretreated corn cob mainly due to the evaporation of both free moisture content and bound water. From Fig. 1 it can be seen that a gradual thermal decomposition process with a significant weight loss for both samples (more than 60%) are observed at a range of temperature from 250 to 400 °C. This significant weight loss of the biomasses mainly due to the thermal decomposition of hemicellulose (200–300 °C) and cellulose (300–360 °C) into smaller molecular weight compounds, such as water, carbon dioxide, carbon monoxide, methane, and other organic compounds. Some of lignin also degraded at this range of temperatures, which mainly due to the breakdown of chemical bonds with low activation energy [12, 14]. The breakdown of more stable bonds in the lignin occurred in temperature range from 400 to 500 °C. At higher temperature (above 500 °C), the weight loss of both biomasses was insignificant as seen in Fig. 1. The chemical compositions of corn cob and its pretreated form which were determined by TGA method are listed in Table 2. Because the corn cob contains high cellulose, this material is suitable as the raw material for levulinic acid production.

The SEM images of natural zeolite and acid modified zeolite are shown in Fig. 2. The modification using acid did not change the surface morphology of zeolite as indicated in Fig. 2. The XRD analysis was used to determine the crystalline structure of zeolite. In general, the modification using hydrochloric acid did not change or alter the crystalline structure of zeolite as shown in Fig. 3. The total surface acidity of natural zeolite was 0.517 mg n-butylamine/g and after modification using hydrochloric acid solution, the total surface acidity increased to 0.815 mg n-butylamine/g. The increase of surface acidity of acid modified zeolite due to the removal of some exchangeable cations (Ca²⁺, Fe³⁺, and Al³⁺) from the framework of zeolite and replaced by H⁺.

The production of levulinic acid from lignocellulosic materials involves several complex reaction mechanisms which also producing several intermediate products. In the hydrolysis process, the cellulose is converted into glucose, while the hemicellulose is converted into hexose (glucose, mannose, and galactose) and pentose (xylose and arabinose). In the dehydration process, hexose will be converted into 5-hydroxy-methylfurfural (HMF) and pentose will be converted into furfural. The decomposition of HMF produces levulinic acid and formic acid. A byproduct produced during the process is humin, black insoluble polymeric materials.

The subcritical water process has unique behavior and has been known as a green process for several applications [13, 15, 16]. Under high temperature and pressure, the water dissociates into H₃O⁺ and OH⁻ ions, and the presence of these excess ions indicates that the water can act as an acid or base catalyst. The subcritical water hydrolysis of pretreated corn cob were conducted either with or without solid acid catalyst additions. The subcritical water hydrolysis products are summarized in Table 3. Without addition of solid acid catalyst, the breakdown of cellulose and hemicellulose into monomeric sugars significantly low as indicated in Table 3.

At subcritical condition the ion products (H₃O⁺ and OH⁻) in water will make the water slightly acidic and at this condition the water become a good solvent for converting cellulose and hemicellulose to sugar monomers. The yield of monomeric sugars (calculated as the amount monomeric sugar/L solution) in the subcritical water process hydrolysis without the presence of catalyst increased with the increase of temperature from 180 to 220 °C (from 1.54 to 2.62 g/L) as seen in Table 3.

At constant pressure, the increase of temperature will decrease the dielectric constant of water and increase the ionization of water into H₂O⁺ and OH⁻ leading to more acidic of the system. The presence of H₂O⁺ (hydroxonium) in the system represents the nature of the proton in aqueous solution and this proton subsequent attacks β-1,4-glycosidic bonds as the linking bonds of several monomeric D-glucose units in the long chain polymer of cellulose, and resulting C₆ sugars as the product. The attack of hydroxonium ions into the linking bond of the hemicellulose chain, resulting C₅ sugars as the product. With the increasing of temperature, the amount of hydroxonium ions also increase, therefore the breakdown of linking bonds of...
The cellulose and hemicellulose became increase leading to the increase of yield of sugars. The addition of solid acid catalyst (modified zeolite) into the system significantly enhanced the breakdown of cellulose and hemicellulose into monomeric sugars (clearly seen in the temperature range of 180°C–220°C). The addition of the acid modified zeolite increased the number of protons (hydroxonium ions from subcritical water and H⁺ from the surface of acid modified zeolite), with the excess number of protons in the solution, the breakdown of linking bonds of the cellulose and hemicellulose became significantly increasing and as the results the yield of monomeric sugars also increases as seen in Table 3.

In the levulinic acid production process, the C₆ sugars were dehydrated to HMF, this intermediate product subsequently converted into LA and formic acid. The C₅

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### Table 2 Chemical composition of corncob and its pretreated form

| Component        | Corncob, wt% | NaOH pretreated corncob, wt% | TGA temperature, °C |
|------------------|--------------|------------------------------|---------------------|
| Water            | 4.3          | 2.8                          | 40–200              |
| Hemicellulose    | 13.1         | 11.3                         | 200–300             |
| Cellulose        | 54.4         | 62.2                         | 300–360             |
| Lignin           | 20.1         | 18.2                         | 360–500             |
| Ash + carbon     | 8.1          | 5.5                          | >500                |

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Fig. 2 SEM images of a natural zeolite, b modified zeolite (1:5), c modified zeolite (1:10), and d modified zeolite (1:15)

Fig. 3 X-Ray diffraction pattern of natural and acid modified zeolite
sugars were converted to furfural, and the later was further degraded into formic acid and other insoluble products [17]. In the first step of dehydration of glucose, the isomerization reaction of glucose-fuctose occurred and subsequently it further dehydrated to HMF and the later converted rapidly to LA and formic acid. The temperature plays important role in the dehydration process of glucose into LA, since all the reactions were endothermic process, the increase of temperature also increases the rate of reaction and the yield of products also increase. At temperature above 180 °C, the isomerization reaction of glucose-fuctose occurred much faster, and more HMF was produced during the process, however, based on the kinetic parameters for the hydrolysis of sugarcane bagasse proposed by Girisuta et al. [17], the formation of LA or dehydration of HMF is much faster than other reactions. As soon as the HMF formed it was instantaneously converted to LA.

To obtain optimum process parameters for the levulinic acid production from corncob using catalytic subcritical water process, the response surface methodology (RSM) was employed to analyze the experimental data. The following polynomial equation was fitted to the response resulted from RSM by the LSM (least square method):

\[ Y = a_0 + \sum_{i=1}^{k} a_i X_i + \sum_{i=1}^{k} a_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} a_{ij} X_i X_j \]  

(1)

where \( Y \) is the concentration of levulinic acid (\( C_{\text{LA}} \)) in the product, \( a_0 \) is a constant coefficient, \( a_i \) are the linear coefficients, \( a_{ij} \) are the interaction coefficients, and \( a_{ii} \) are the quadratic coefficients. \( X_i \) and \( X_j \) are the codec values of the variables. The independent variables used in this study were ratio of zeolite and acid (\( R \)), temperature (\( T \), °C), and reaction time (\( t \), min). The regression model was calculated using Minitab 16.1.1 Statistical software to estimate the response of dependent variables. The analysis of variance (ANOVA) was employed to confirm the adequacy of the model parameters. The suitability of the model to represent the data was determined by the value of \( R^2 \).

The full quadratic model that describes the relationship between the effects of ratio of zeolite and acid (\( R \)), temperature (\( T \), °C), and reaction time (\( t \), min) on the concentration of levulinic acid is given as follow

\[
C_{\text{LA}} = 37102.7 + 5393.3R + 3893.3T \\
+ 6040.8t - 254.5R^2 - 14713.5T^2 + 1485.8t^2 \\
+ 689.4RT + 1993.5Tt - 1039.5T^2 \\
(2)
\]

\( p \) value of the quadratic model (<0.0001) was significant at the probability level of 5 % (\( R^2 = 0.9614 \)). The first order effect of variables \( R, T \), and \( t \) on the output parameter \( C(\text{LA}) \) were significant at the confidence level of 95 %. However, the second order effect of \( R \) and \( t \) as well as the interactions between \( R \) and \( t \), \( R \) and \( T \), and \( T \) and \( t \) were insignificant as indicated in Table 4. Re-arrangement of Eq. (2) with the inclusion only the significant parameters give the following result:

\[
C_{\text{LA}} = 37102.7 + 5393.3R + 3893.3T \\
+ 6040.8t - 14713.5T^2. \\
(3)
\]

The effects of ratio of zeolite and acid (\( R \)), temperature (\( T \)) and time (\( t \)) of subcritical water hydrolysis on the concentration of levulinic acid are plotted as surface plots in Figs. 4, 5 and 6. Both of these parameters have positive effects on the yield of levulinic acid (concentration). As mentioned before that temperature play important role both in hydrolysis and hydration processes, by increasing temperature the formation of levulinic acid or dehydration of HMF is much faster than other reactions. However, if the temperature is too high and the activation energy of the formation of humin is achieved, the degradation of HMF into humin is faster than the dehydration of HMF into levulinic acid and this phenomenon decreases the yield of levulinic acid. By increasing the subcritical hydrolysis time, the contact between the cellulose and hemicellulose with the ionic product of water (\( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \)) become more intense and longer, and more of the cellulose and hemicellulose molecules were hydrolyzed and converted into monomeric sugars and subsequently dehydrated into HMF and levulinic acid. The ratio of zeolite and

| Temperature, °C | Acid activated zeolite, g | Yield mg/g dried corncob |
|----------------|---------------------------|-------------------------|
|                | Glucose | Xylose | Galactose | Arabinose |
| 180            | 2.40    | 4.05   | 0.85     | 0.40      |
|                | 55.65   | 40.20  | 27.40    | 14.55     |
| 200            | 6.05    | 4.60   | 1.05     | 0.55      |
|                | 82.55   | 57.75  | 42.55    | 36.10     |
| 220            | 7.60    | 4.55   | 0.55     | 0.40      |
|                | 120.65  | 76.90  | 47.60    | 42.20     |

Table 3 Monomeric sugars in subcritical water hydrolysis product
hydrochloric acid also had a positive effect on the concentration of levulinic acid, by increasing of the ratio of acid, the ion exchange between some metal cations with H\(^+\) also increased. Subsequently, with the increased of H\(^+\) in the surface of zeolite catalyst also increased the number of protons in the solution leading to the increase of the breakdown of linking bonds of the cellulose and hemicellulose to produce monomeric sugars. These monomeric sugars under acidic condition and high temperature were dehydrated into levulinic acid.

The experimental results of the effects of temperature, reaction time, and the ratio of zeolite and hydrochloric acid (activation of zeolite) on the yield of levulinic acid are given in Table 5.

To obtain the maximum yield or concentration of levulinic acid is an important point in this study to establish an efficient process. This objective can be achieved through the setting of all significant parameters at optimum conditions. The optimum condition of the production of levulinic acid from corncob through subcritical water process is depicted in Fig. 7. RSM indicates the optimum conditions for the variable of ratio of zeolite and acid was coded 1, variable of hydrolysis temperature was coded 0.1111 and hydrolysis time was coded 1. These units

| Source      | DF | Seq SS     | Adj SS     | Adj MS     | F    | p value |
|-------------|----|------------|------------|------------|------|---------|
| Regression  | 9  | 1,498,173,667 | 1,498,173,667 | 166,463,741 | 39.05 | 0.000   |
| Linear      | 3  | 645,895,733  | 645,895,733 | 215,298,578 | 50.51 | 0.000   |
| R           | 1  | 232,702,558  | 232,702,558 | 232,702,558 | 54.59 | 0.001   |
| T           | 1  | 121,263,058  | 121,263,058 | 121,263,058 | 28.45 | 0.000   |
| t           | 1  | 291,930,117  | 291,930,117 | 291,930,117 | 68.48 | 0.000   |
| Square      | 3  | 830,159,318  | 830,159,318 | 276,719,773 | 64.91 | 0.000   |
| R\(^2\)     | 1  | 5,369,842    | 239,105    | 239,105    | 0.06  | 0.822   |
| T\(^2\)     | 1  | 816,638,331  | 799,339,635 | 799,339,635 | 187.51 | 0.000   |
| t\(^2\)     | 1  | 8,151,145    | 8,151,145  | 8,151,145  | 1.91  | 0.225   |
| Interaction | 3  | 22,118,617   | 22,118,617 | 7,372,872  | 1.73  | 0.276   |
| RT          | 1  | 1,900,814    | 1,900,814  | 1,900,814  | 0.45  | 0.534   |
| Rt          | 1  | 15,895,770   | 15,895,770 | 15,895,770 | 3.73  | 0.111   |
| Tt          | 1  | 4,322,033    | 4,322,033  | 4,322,033  | 1.01  | 0.360   |
| Residual error | 5  | 21,314,232   | 21,314,232 | 4,262,846  | 10.22 | 0.090   |
| Lack-of-fit | 3  | 20,009,560   | 20,009,560 | 6,669,853  | 10.22 | 0.090   |
| Pure error  | 2  | 1,304,673    | 1,304,673  | 652,336    |      |         |
| Total       | 14 | 1,519,487,900|          |            |      |         |
correlate to zeolite and an acid ratio of 1:15, reaction temperature of 200 °C, and reaction time of 60 min and correspond to the optimum concentration of levulinic acid of 52,480 ppm (262.4 mg/g dried corncob). To test the validity of the optimum condition obtained from the RSM, an experiment has also been conducted using process variables values from the RSM, and as the result the concentration of levulinic acid of 53,989.7 ppm (269.9 mg/g) was obtained. Since the difference between the experiment and the optimize value from RSM only 2.8 %, therefore, these theoretical optimum values obtained from RSM are considered to be appropriate.

The stability and reusability of the heterogeneous catalyst are crucial issues for industrial application. To examine the stability and reusability of acid modified zeolite, the catalyst was recovered from the reaction mixture, re-calcined at 400 °C for 4 h, and reused five times. The reaction temperature of 200 °C, reaction time of 60 min, and zeolite to acid ratio of 1:15 were used as the reaction parameters to study of the reusability of catalyst. The reusability results of the spent catalyst are depicted in Fig. 8. This figure clearly shows that the yield of levulinic acid gradually decrease after the first run. This phenomenon indicates that the catalyst has gradually deactivated during the reaction.

### Table 5 The effect of temperature and reaction time on the yield of levulinic acid

| Temperature, °C | Time of hydrolysis, min | Ratio zeolite: volume HCl, g:ml | Yield of levulinic acid, mg/g dried corncob |
|-----------------|-------------------------|---------------------------------|---------------------------------------------|
| 180             | 30                      | 1:10                            | 73.8                                        |
| 180             | 45                      | 1:5                             | 69.5                                        |
| 180             | 45                      | 1:15                            | 114.7                                       |
| 180             | 60                      | 1:10                            | 129.3                                       |
| 200             | 30                      | 1:5                             | 138.4                                       |
| 200             | 30                      | 1:15                            | 174.3                                       |
| 200             | 45                      | 1:10                            | 181.9                                       |
| 200             | 60                      | 1:5                             | 194.2                                       |
| 200             | 60                      | 1:15                            | 269.9                                       |
| 220             | 30                      | 1:10                            | 119.8                                       |
| 220             | 45                      | 1:5                             | 104.9                                       |
| 220             | 45                      | 1:15                            | 163.9                                       |
| 220             | 60                      | 1:10                            | 154.4                                       |
The activation of catalyst during the reaction cycle due to the leaching of surface acid sites (the acidity of fresh catalyst was 0.815 mg n-butyramine/g and after 5th cycle was 0.423 mg n-butyramine/g) and the formation of humin in the active sites of the catalyst.

Conclusion

Cornocob had been successfully used as the new raw material for levulinic acid production. The production of levulinic acid was conducted in subcritical condition with the presence of acid modified zeolite as catalyst. The yield of levulinic acid in the final product was strongly influenced by the ratio of zeolite and acid, reaction temperature, and reaction time. The optimum yield of levulinic acid was 262.4 mg/g dried corncob, and was obtained at temperature of 200 °C, reaction time of 60 min, and zeolite to acid ratio of 1:15.

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Authors’ contributions CDH, KJM and JNP conducted the experiments, while DANS performed the statistical analysis, FES and YHJ drafting the manuscript, SI performed the experiment design and corrected the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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