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0086-8 RESEARCH Levulinic acid from corncob by subcritical water process Chynthia Devi Hartono1 • Kevin Jonathan Marlie1 • Jindrayani Nyoo Putro2 • Felycia Edi Soetardjo1 • Yi Hsu Ju2 • Dwi Agustin Nuryani Sirodj3 • Suryadi Ismadji1 Received: 7 October 2015 / Accepted: 17 May

12**2016 / Published online:** 27 May **2016 ? The Author(s) 2016. This article is published with open access at Springerlink.com Abstract The** productions **of**

levulinic acid from corncob were carried out by subcritical water process in a temper- ature 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 modifi- cation 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 & Suryadi Ismadji suryadiismadji@yahoo.com Felycia Edi Soetardjo felyciae@yahoo.com 1

5**Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia** 2 **Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Rd, Taipei 106, Taiwan,** People’s Republic **of**

China 3

3**Department of** Industrial **Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia**

Introduction Levulinic acid

8**(4-oxopentanoic acid or** c **-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

6**for the** production **of various organic compounds.** It **can be used**

for the production of polymers, resins, fuel additives, fla- vors, 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 levu- linic 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 lignocellu- losic biomass [2–4, 7–9]. Usually, the homogeneous cata- lysts are more effective than some of heterogeneous catalysts; however, the drawbacks of the use of homoge- neous catalysts for levulinic acid production are associated with the corrosion of the equipment, environmental prob- lem, 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

10**conversion of sugars into levulinic acid**

[3]. Zeolite- type materials, such as faujasite and modernite, have

16**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

10**for levulinic acid production** [12]. **The** production **of levulinic acid**

from agricultural waste materials involves two critical steps of processes; the first process is hydrol- ysis, in the hydrolysis process the hemicellulose and cel- lulose 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].

9**In this** study, **the production of levulinic acid from**

corncob was conducted on subcritical water condition using acid modified zeolite as heterogeneous catalyst.

24**Subcritical water (SCW)** process **is** an **environmentally friendly** method, which **can be** applied in various applica- tions, such as

24**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 lead to the increase of the hydrolysis and dehydration rate of reactions and subsequently increases the yield of levulinic acid.

18**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 levu- linic 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 Corncobs 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

25**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

7**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 (H_2O_2) 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 SiO_2 (60.14 %), Al_2O_3 (12.52 %), CaO (2.51 %), Fe_2O_3 (2.49 %), Na_2O (2.44 %), K_2O (1.28 %), MgO (0.49 %), H_2O (14.40 %), and loss on ignition (3.73 %).

25**All chemicals used in this study, such as**

sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), 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/vol- ume). Thirty grams of zeolite powder were mixed with a certain volume of HCl solution and transferred

18**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

3**was separated from the** mixture **by vacuum filtration** system. **The** solid **was**

repeatedly washed with distilled Table 1 Proximate and ultimate analysis of corncob and its pre- treated form Component Corncob, wt% NaOH pretreated corncob, wt% Ultimate analysis (dry basis) Carbon 54.1 Hydrogen 6.8 Nitrogen 0.3 Sulfur 0.1 Oxygen 38.7 Proximate analysis (dry basis) Moisture content 10.4 Volatile matter 67.1 Fixed carbon 19.4 Ash 3.1 53.8 6.9 0.2 0.1 39.0 10.1 71.8 15.2 2.9 403 water to remove the excess HCl solution. The acid modi- fied zeolite was dried in oven at 110 ?C for 24 h to remove free moisture content. Then, modified zeolite was calcined in a furnace

13**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

3**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 con- ducted 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,

5**type K thermocouple, and M8 screws for** tighten- ing **the reactor with its cap. The**

maximum allowable temperature and pressure of the vessel are 250 ?C and 100 bar, respectively. The reaction experiments were conducted at a pressure of 30 bar and three different tem- peratures (180, 200, and 220 ?C). The typical reaction experiment is briefly described as follows:

17**20 g of** corncob **powder** were **mixed with 100 ml of**

distilled water; sub- sequently 0.5 g of acid modified zeolite was added into the mixture. The mixture was heated until the desired tem- perature was reached, and during the heating process, the nitrogen gas was introduced to the system to maintain the water in the liquid condition.

3**During the** reaction **process, the mixture was stirred at**

300 rpm. After the hydrolysis time was reached (30, 45, and 60 min), the reactor was rapidly cooled to room temperature. The solid was sepa- rated from the liquid by centrifugation at 3000 rpm. The concentrations of levulinic acid and other organic sub- stances, such as sugars, organic acids and HMF, were determined by high performance liquid chromatography (HPLC) analysis. Characterization of corncob and zeolite The chemical composition of the corncob and delignified corncob was determined using Thermal gravimetric Analysis (TGA). The

19**analysis was performed** on **a TGA/ DSC-1 star system (Mettler-Toledo) with** ramping **and cooling rate of 10** ?C **/min**

21**from room temperature to 800 ?C** under continuous **nitrogen** gas flow **at**

a flowrate of 50 ml/min. The mass of the sample in each measurement was 10 mg. The surface topography of the corncob and zeolite cat- alysts was characterized using a field emission Scanning Electron Microscope (SEM), JEOL JSM 6390 equipped with backscattered electron (BSE) detector at an acceler- ating voltage of 15 and 20 kV at a working distance of 12 mm. Prior to SEM analysis, an ultra-thin layer of con- ductive platinum was sputter-coated on the samples using an auto fine coater (JFC-1200, JEOL, Ltd., Japan) for 120 s in an argon atmosphere. The

22**X-ray powder diffraction (XRD) analysis of the samples was performed on a** Philips PANalytical **X'** Pert powder X **-ray diffractometer with**

a monochromated high intensity Cu Ka1 radiation (k = 1.54056 Å). The XRD was operated

17**at 40 kV,** 30 **mA, and a step size of 0.**

05?/s from the 2h angle between 5 and 90?. The surface acidity of the zeolite acid activated zeolite was determined by amine adsorption analysis.

3**A brief description of the** method **is as follows:**

a known amount of air dried zeolite or acid activated zeolite (50 mg) were added into a series of test tubes. Subsequently, different volumes (20–50 ml) of n-butylamine solution in benzene (0.01 M) were added to the test tubes. The test tubes then tightly stoppered and stores at 30 ?C. After the equilibrium condition was achieved, the remaining n-butylamine in the solution was determined by titration using 0.016 M tri-chloroacetic acid solution in benzene, and 2,4 dinitrophe- nol was used as the indicator. HPLC analysis The organic compounds in the aqueous phase of the pro- duct 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 injec- tion in the HPLC system, all of the liquid

16**samples were filtered through a 0.** 22 lm PVDF **syringe filter. The**

anal- ysis of monomeric sugars was conducted with an Aminex HPX-87P sugar column (Bio-Rad, 300 9 7.8 mm) using degassed

8**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

26**Bio-Rad Aminex HPX- 87H column (300 9 7.8 mm) was used** as **the** separating column. **The**

isocratic elution of sulfuric acid aqueous solution (5 mM)

15**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 corncob and sodium hydroxide treated corncob, the thermal gravimetric Analysis (TGA) was conducted under the nitrogen envi- ronment. The TGA curves of both samples are given in Fig. 1. At temperature between 50 and 200 ?C, the weight loss of corncob and the pretreated corncob 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 decom- position 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 degra- ded 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 corncob and its pretreated form which were determined by TGA method are listed in Table 2. Because the corncob 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

3**XRD analysis was** used **to** determine **the crystalline structure of**

zeolite. In general, the modification using hydrochloric acid did not change or alter the crys- talline structure of zeolite as shown in Fig. 3. The total 100 80 Corncob Wt, % 60 Pretreated corncob 40 20 0 0 200 400 600 800 Temperature, oC Fig. 1 Thermogravimetric curve of corncob and NaOH pretreated corncob surface acidity of natural zeolite was 0.517 mg n-buty- lamine/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 arabi- nose). In the dehydration process, hexose will be converted into 5-hydroxy-methylfurfural (HMF) and pentose will be converted into furfural. The decomposition of HMF pro- duces levulinic acid and formic acid. A byproduct pro- duced 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].

23**Under high temperature and** pressure, the **water dissociates into** H3O? **and OH- ions,**

and the pres- ence of these excess ions indicates that the water

23**can act as** an **acid or base catalyst.**

The subcritical water hydrolysis of pretreated corncob 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 con- verting cellulose and hemicellulose to sugar monomers. The yield of monomeric sugars (calculated as the amount monomeric sugar/L solution) in the subcritical water pro- cess 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 H3O? and OH- leading to more acidic of the system. The presence of H3O? (hydroxonium) in the system represents the nature of the proton in aqueous solution and this proton subsequent attacks b-1,4-glyco- sidic 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 hydrox- onium 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 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

21**Fig. 2 SEM images of a** natural **zeolite, b** modified **zeolite**

(1:5), c modified zeolite (1:10), and d modified zeolite (1:15) Intensity Natural zeolite 1:5 1:10 1:15 0 10 20 30 40 50 2θ, o Fig. 3 X-Ray diffraction pattern of natural and acid modified zeolite 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?–220?). The addition of the acid modified zeolite increased the number of pro- tons (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 signifi- cantly 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 sub- sequently converted into LA and formic acid. The C5 Table 3 Monomeric sugars in subcritical water hydrolysis product Temperature, ?C Acid activated zeolite, g Yield mg/g dried corncob Glucose Xylose Galactose Arabinose 180 0 0.5 2.40 55.65 4.05 40.20 0.85 27.40 0.40 14.55 200 0 0.5 6.05 82.55 4.60 57.75 1.05 42.55 0.55 36.10 220 0 0.5 7.60 120.65 4.55 76.90 0.55 47.60 0.40 42.20 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 iso- merization reaction of glucose-fructose occurred and sub- sequently 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 tem- perature above 180 ?C, the isomerization reaction of glu- cose-fructose occurred much faster, and more HMF was produced during the process, however, based on the

6**kinetic parameters for the hydrolysis of** sugarcane **bagasse**

pro- posed by Girisuta et al. [17], the formation of LA or dehydration of HMF is much faster than other reactions.

6**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 fol- lowing polynomial equation was fitted to the response resulted from RSM by the LSM (least square method): X k X aiiX2i þ Xk?1 X k k Y ¼ ao þ aiXi þ aijXiXj ð1Þ i?1 i?1 i¼1 j¼iþ1 where Y is the concentration of levulinic acid (CLA) in the product, ao is a

> 14**constant coefficient, al** are **the linear coefficients, aij** are **the interaction coefficients,** and **aii** are **the quadratic coefficients.** Xi and Xj **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

> 13**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 R2. The full quadratic model that describes the relationship between the effects of ratio of zeolite and acid (R), tem- perature (T, ?C), and reaction time (t, min) on the con- centration of levulinic acid is given as follow CLA ¼ 37102:7 þ 5393:3 R þ 3893:3 T þ 6040:8 t?254:5 R2? 14713:5 T2 þ 1485:8 t2 þ 689:4 RT þ 1993:5 Rt?1039:5 Tt: ð2Þ p value of the quadratic model (\0.0001) was significant at the probability level of 5 % (R2 = 0.9614). The first order effect of variables R, T, and t on the output parameter (CLA) 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, 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: CLA ¼ 37102:7 þ 5393:3 R þ 3893:3 T þ 6040:8 t?14713:5 T2: ð3Þ 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 tem- perature 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 (H3O? and 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 Table 4 Analysis of variance for concentration

> 9**of levulinic acid as a function of** ratio **of** zeolite and **acid**

(R), temperature (T, ?C), and reaction time (t, min)

11**Source DF Seq SS Adj SS Adj MS F p** value **Regression Linear** R T t **Square** R2 T2 t2 **Interaction** RT Rt Tt **Residual error Lack-of-fit Pure error Total 9**

1,498,173,667 3 645,895,733 1 232,702,558 1 121,263,058 1 291,930,117 3 830,159,318 1 5,369,842 1 816,638,331 1 8,151,145 3 22,118,617 1 1,900,814 1 15,895,770 1 4,322,033 5 21,314,232 3 20,009,560 2 1,304,673 14 1,519,487,900 1,498,173,667 645,895,733 232,702,558 121,263,058 291,930,117 830,159,318 239,105 799,339,635 8,151,145 22,118,617 1,900,814 15,895,770 4,322,033 21,314,232 20,009,560 1,304,673 166,463,741 215,298,578 232,702,558 121,263,058 291,930,117 276,719,773 239,105 799,339,635 8,151,145 7,372,872 1,900,814 15,895,770 4,322,033 4,262,846 6,669,853 652,336 39.05 50.51 54.59 28.45 68.48 64.91 0.06 187.51 1.91 1.73 0.45 3.73 1.01 10.22 0.000 0.000 0.001 0.000 0.000 0.000 0.822 0.000 0.225 0.276 0.534 0.111 0.360 0.090 Fig. 4 Surface plot of concentration levulinic acid as a function of temperature and time of subcritical water hydrolysis Fig. 5 Surface plot of concentration

9**levulinic acid as a function of** ratio **of** zeolite and **acid,**

and time of subcritical water hydrolysis hydrochloric acid also had a positive effect on the con- centration 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 Fig. 6 Surface plot of concentration levulinic acid a function of ratio of zeolite and acid, and temperature of subcritical water hydrolysis of protons in the solution leading to the increase of the breakdown of linking bonds of the cellulose and hemicel- lulose 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 con- ditions. 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 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 Fig. 7 Independent factor optimization during subcritical water hydrolysis and hydration processes of corncob correlate to zeolite and an acid ratio of 1:15, reaction

7**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 con- centration 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 cata- lyst are crucial issues for industrial application. To exam- ine the stability and reusability of acid modified zeolite, the catalyst was recovered from the reaction mixture, re-cal- cined at 400 ?C for 4 h, and reused five times. The reaction

7**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 fig- ure 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 300 Yield, mg/g dried corncob 250 Levulinic acid 200 150 100 50 0 Fresh 1st reuse 2nd reuse 3rd reuse 4th reuse 5th reuse Number of reuse Fig. 8 The stability and reusability of spent catalyst cycle. 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-butylamine/g and after 5th cycle was 0.423 mg n-butylamine/g) and the formation of humin in the active sites of the catalyst. Conclusion Corncob had been successfully used as the new raw material

10**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, reac- tion time of 60 min, and zeolite to acid ratio of 1:15. Acknowledgments The financial support from The World Academy of Science Research Grant 2015/2016 with contract no 14-095/RG/ CHE/AS-1; UNESCO FR:325028591 and LPPM Widya Mandala Surabaya Catholic University through Outstanding Lecturer Research Grant 2014/2015 with contract number 845a/WM01.5/N/2014 is gratefully acknowledged. Authors' contributions CDH, KJM and JNP conducted the experi- ments, while DANS performed the statistical analysis, FES and YHJ drafting the manuscript, SI performed the experiment design and corrected the

1**manuscript. Compliance with ethical standards Conflict of interest The authors declare that** they **have no competing interests. Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://** crea tivecommons **.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.**

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