Catalytic Conversion of Lignocellulosic Biomass to Levulinic Acid in Ionic Liquid

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The catalytic conversion of lignocellulosic biomass to levulinic acid in ionic liquid, [EMIM][Cl] was conducted using a hybrid catalyst. The hybrid catalyst (1:1 ratio) with equal $CrCl_3$ and HY zeolite weight ratios was synthesized using a wet impregnation method. Initially, optimization of cellulose as a model compound was carried out using two-level full factorial design (2^3) with two centre points. Under optimum process conditions, 46.0% of levulinic acid yield was produced from cellulose. Subsequently, utilization of lignocellulosic biomass demonstrated 15.5% and 15.0% of levulinic acid yield from empty fruit bunch (EFB) and kenaf, respectively, at the optimum conditions. Meanwhile, in the presence of ionic liquid under the same process conditions, 20.0% and 17.0% of levulinic acid were obtained for EFB and kenaf, respectively. The results indicated that ionic liquid could disrupt the covalent linkages between the biomass structures and dissolved the hollocellulose. This allowed the hollocellulose chains, accessible to the chemical transformation, to react and produce levulinic acid in presence of the hybrid catalyst. This study demonstrated that the combination of hybrid catalyst and ionic liquid has the potential to be applied for biomass conversion to levulinic acid under adequate process conditions.

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INTRODUCTION

With increasing petroleum oil prices, it is inevitable for the chemical industries to seek alternative raw materials for basic chemical production (Fang and Hanna 2002). Biomass is the only renewable resource with fixed carbon, which is essential for the production of fuel and bio-based chemical products (Girisuta 2007). One of the versatile bio-based chemicals is levulinic acid, a short chain fatty acid having a ketone carbonyl group and a carboxylic acid group; this can be used as a building block for various bulk chemicals (Chen *et al.* 2011). Levulinic acid is an intermediate to the γ-valerolactone (GVL), which is an ideal sustainable liquid, since it can be converted into both energy and carbon-based products (Gong *et al.* 2011).

A number of approaches have been reported for levulinic acid production, including acid-catalyzed dehydration and hydrolysis of biomass and carbohydrates (Galleti *et al.* 2012; Girisuta 2007). Due to the problems associated with homogeneous acid catalysts, heterogeneous acid catalysts seem a feasible alternative. The heterogenous catalytic system has several advantages, including selective, recyclable and regeneration abilities, and it is also easier to separate (Chen *et al.* 2011; Rackemann and Doherty 2011). However, low levulinic acid yields were reported previously under prolonged

reaction time and high reaction temperature (Jow *et al.* 1987; Lourvanij and Rorrer 1993; Zeng *et al.* 2010). Therefore, further studies on better reactive catalysts are still needed to comprehend the catalytic activities for the formation of levulinic acid from biomass sources.

Hybrid catalysts consisting of zeolite and metal halide salt are rarely utilized in biomass processing, especially in levulinic acid production. As reported by Ya'aini *et al.* (2013), a hybrid catalyst was synthesized through modification of HY zeolite by introducing $CrCl_3$. The catalytic activity of the hybrid catalyst for cellulose conversion revealed that the reactions were predominantly influenced by the type and strength of acid sites (Lewis acid), surface area, hierarchical porous structures, and shape selectivity properties (Ya'aini *et al.* 2013).

Moreover, a new pathway for biomass conversion to value-added products in a single process under mild conditions can be developed by catalytic hydrolysis in ionic liquid (Lee *et al.* 2011; Wang *et al.* 2011). Ionic liquids are versatile green solvents that can act as solvents, as catalysts, and be utilized in many different ways (Olivier-Bourbigou *et al.* 2010).

Recently, ionic liquids have been used as a reaction medium by combining with solid acid, metal halide, or salts and mineral acid in biomass hydrolysis and dehydration processes to produce 5-hydroxymethylfurfural, HMF, the intermediate product of levulinic acid (Hu *et al.* 2009; Li *et al.* 2009; Su *et al.* 2009; Zhang and Zhao 2009).

To date there have been few reports of the potential use of these treatment methods for producing levulinic acid. Thus, this study employed the combination of low cost biomass sources with a new hybrid catalyst in ionic liquid medium for levulinic acid production.

EXPERIMENTAL

Materials

HY zeolite ($SiO_2/Al_2O_3 = 30$) was purchased from Zeolyst International Inc. Chromium chloride ($CrCl_3$) was supplied by Merck, Germany, while sulfuric acid (H_2SO_4) 95–97% was purchased from QRec, New Zealand. Standard analytical grade of levulinic acid 98% (Sigma Aldrich) was used for the analysis of the desired products, while deionized water was used for the solution reactions.

Empty fruit bunch was supplied by Malaysia Palm Oil Board (MPOB), Kuala Lumpur, Malaysia. Meanwhile, kenaf was supplied by the Polymer Engineering Department, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, Malaysia. The samples were dried overnight at 105 °C in the oven. The dried samples were later grinded and reduced to small size particles (less than 1.0 mm).

Experimental Design

A two-level factorial design was used to identify the factors that have significant effect in the catalytic reactions of cellulose conversion into levulinic acid. The effects of x_1 (reaction temperature), x_2 (reaction time) and x_3 (catalyst loading) were selected at three different levels. These levels were low (-1), medium (0), and high (1), respectively, as tabulated in Table 1. This designed experiment was carried out using Statsoft Statistica 8.0 software.

Table 1. Experimental Range and Levels for the Independent Variables

Factors	Symbol		Range & Level		
	Uncoded	Coded	-1	0	+1
Temperature, (ºC)	X_1	x_1	100	150	200
Time, (min)	X_2	x_2	60	120	180
Catalyst loading, (g)	X_3	x_3	1	8	10

Experimental Procedures

The methods for hybrid 1:1 catalyst preparation and biomass characterization were according to the procedures reported elsewhere (Ya'aini *et al.* 2012). The cellulose sample (0.1 g) in [EMIM][Cl] ionic liquid (1.5 g) was mixed in a closed 150 mL Scott bottle (batch reactor). Then, the batch reaction system was immersed in the preheated silicon oil at 100 °C and atmospheric pressure until a clear solution was formed under continuous stirring at a speed of 300 rpm. Next, the solution was loaded with an appropriate amount of hybrid catalyst according to the experimental design and stirred at various reaction temperatures and reaction times. Immediately after the reaction was completed, 10 mL of deionized water was added to the solution at room temperature. The reaction mixture was briskly stirred to rehydrate and dissolve the water-soluble reaction products away from the solid hybrid catalyst and humin. All the samples were filtered through a 0.45 µm membrane syringe filter and the liquid phase was further analyzed using high performance liquid chromatography (HPLC). Similar steps were further applied for the utilization of EFB and kenaf at the optimum conditions.

Analysis Methods

The concentration of liquid phase samples were determined by using a model of Perkin Elmer Series 200 instrument (HPLC) under the following conditions: column, organic acid Aminex HPX-87H; flow rate, 0.6 mL/min; mobile phase, H_2SO_4 (5 mM); detector, UV_{210nm}; retention time, 60 min; and column temperature, 60 ºC. The concentration of the samples was determined using a prepared standard levulinic acid calibration curve with known concentration. The levulinic acid yield was calculated as in Eq. 1:

$$\text{Levulinic acid yield (wt\%)} = \frac{\text{weight of product (g)}}{\text{initial weight of feedstock (g)}} \times 100\% \qquad (1)$$

RESULTS AND DISCUSSION

Statistical Analysis

Optimization of levulinic acid from cellulose was conducted in [EMIM][Cl] ionic liquid as the solvent. Based on the literature review screening, [EMIM][Cl] ionic liquid is the most effective and appropriate solvent for dissolving cellulose. Fractionation of cellulose structures is required to release the sugars (glucose, fructose) before they can be further converted to produce levulinic acid (Rackemann and Doherty 2011). Cellulose was used as a model compound prior to utilizing the lignocellulosic biomass samples in this study. Cellulose, composed of D-glucose monomers and joined together by β–1,4–glycosidic bonds, could be converted into glucose by using ionic liquid as a medium to

depolymerize the cellulose. Many studies have reported the effectiveness of ionic liquid in dissolving cellulose. Ionic liquids containing chloride anion have a high tendency to solubilize cellulose compared to other anions (Olivier-Bourbigou *et al.* 2010; Wang *et al.* 2011). Utilization of the hybrid catalyst in ionic liquid was sufficiently demonstrated in cellulose conversion to levulinic acid in this study. In the cellulose optimization process, the experimental matrix for the design and analytical results of the levulinic acid yield is shown Table 2. Meanwhile, the proposed model for the response is given in Eq. 2:

$$Y = -77.2025 + 1.1026x_1 + 0.3343x_2 + 0.2256x_3 - 0.0034x_1^2$$
$$- 0.0011x_2^2 + 0.0136x_3^2 + 0.0003x_1x_2 - 0.0069x_2x_3 + 0.0088x_2x_3 \qquad (2)$$

Table 2. Experimental Design and Analysis Results of Cellulose

Run	Variables						Response
	x_1		x_2		x_3		Y
	Reaction temperature (ºC)		Reaction time (min)		Catalyst loading (0.1 x_3 g)		Levulinic acid yield (%)
1	100	-1	60	-1	1	-1	18.8
2	100	-1	60	-1	10	+1	20.1
3	100	-1	180	+1	1	-1	29.2
4	100	-1	180	+1	10	+1	37.5
5	200	+1	60	-1	1	-1	28.9
6	200	+1	60	-1	10	+1	30.6
7	200	+1	180	+1	1	-1	44.6
8	200	+1	180	+1	10	+1	50.2
9	150	0	120	0	8	0	41.8
10	62	-α	120	0	8	0	14.4
11	238	+α	120	0	8	0	14.5
12	150	0	14	-α	8	0	5.0
13	150	0	226	+α	8	0	52.1
14	150	0	120	0	0.1	-α	36.0
15	150	0	120	0	16	+α	47.1
16	150	0	120	0	8	0	45.8

The proposed model showed a close agreement between the observed and predicted results, where the coefficient of determination (R^2) at 0.9119 for the levulinic acid yield was close to unity (Fig. 1). This result indicated that 91.19% of the variability in the response can be explained by the model. Only 8.81% of the total variability was not explained in the model. Therefore, the proposed model adequately explained most of the variability in the statistical analysis for cellulose. The analysis of variance (ANOVA) as tabulated in Table 3 shows that the *F*-value for levulinic acid yield was 6.90. The *F*-value was higher than the tabulated *F*-value ($F_{0.05,9,6}$) by rejecting the null hypothesis at the 0.05 level of significance where the tabulated *F*-value is used at a high confidence level (95%) in order to obtain a good prediction model.
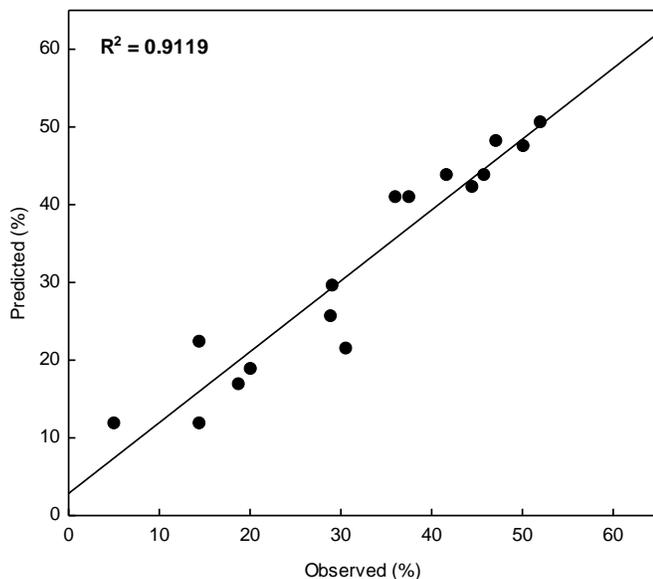
Fig. 1. The coefficient of determination and predicted versus observed values for levulinic acid yield from cellulose

Table 3. Analysis of Variance (ANOVA) for Quadratic Model

Sources	SS	Df	MS	F_{value}	$F_{0.05}$
Regression	2857.71	9	317.52	6.90	>2.74
Residual	275.99	6	46.00		
Total	3133.70	15			

SS, sum of squares; Df, degrees of freedom; MS, mean square.

Meanwhile the significance of each coefficient was determined by Pareto chart (Fig. 2).

Fig. 2. Pareto chart of levulinic acid yield

As shown, the linear coefficients of reaction time, x_2 and quadratic coefficient of reaction temperature, x_1^2 had significantly effects on the levulinic acid yield with the largest t-value (5.1612, 4.1886) and smallest p-value (0.0021, 0.0058), respectively. This suggested that the reaction time followed by reaction temperature were the two variables that affected the conversion process most. Furthermore, the quadratic coefficient of catalyst loading, x_3^2 gave the least effect on the levulinic acid yield in this reaction process.

Variable Effects on the Response

The interaction effects of the variables on the response for cellulose conversion are illustrated in 3D response surface plots (Figs. 3 to 5). Figure 3 depicts the relative significant interaction between the reaction time and reaction temperature at fixed 0.7 g catalyst loading. The levulinic acid yield linearly increased with increasing reaction time.
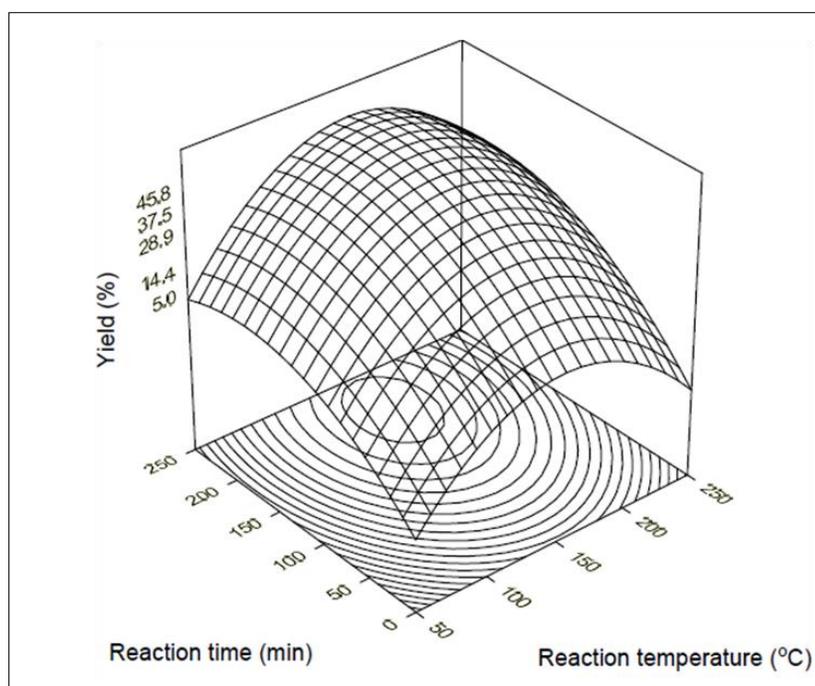

Fig. 3. 3D response surface plot of levulinic acid yield versus reaction time and reaction temperature

Meanwhile, the levulinic acid yield initially increased with an increase in reaction temperature but decreased beyond a certain point. With the increasing of reaction temperature, the reaction rate of cellulose conversion increased, but above the optimum condition the levulinic acid yield decreased due to the formation of unwanted side reactions. Increasing reaction temperature accelerated the conversion rate due to enhanced cellulose solubility at higher temperature (Hegner *et al.* 2010). These linear and quadratic trends of reaction temperature and time on levulinic acid yield were consistent with previous analysis (Pareto chart). Therefore, a high levulinic acid yield could be obtained from cellulose at moderate reaction temperature and longer reaction time.

Figure 4 illustrates the interaction of reaction time and catalyst loading for the cellulose conversion into levulinic acid at 150 °C of reaction temperature. At a given reaction temperature, longer reaction time and higher catalyst loading enhanced the

levulinic acid production. Longer reaction time allowed the cellulose to be converted into levulinic acid while high catalyst loading provided more reactive sites in the reaction process. Levulinic acid was not detected without the presence of catalyst and ionic liquid. This demonstrated that the interaction of hybrid 1:1 catalyst with cellulose in the presence of [EMIM][Cl] ionic liquid had a positive effect on the formation of levulinic acid. Ionic liquid with chloride as the anion makes it possible to balance solubility of cellulose and hydrolytic activity by strong interactions with cellulose coupled with weak basicity (Binder and Raines 2010).
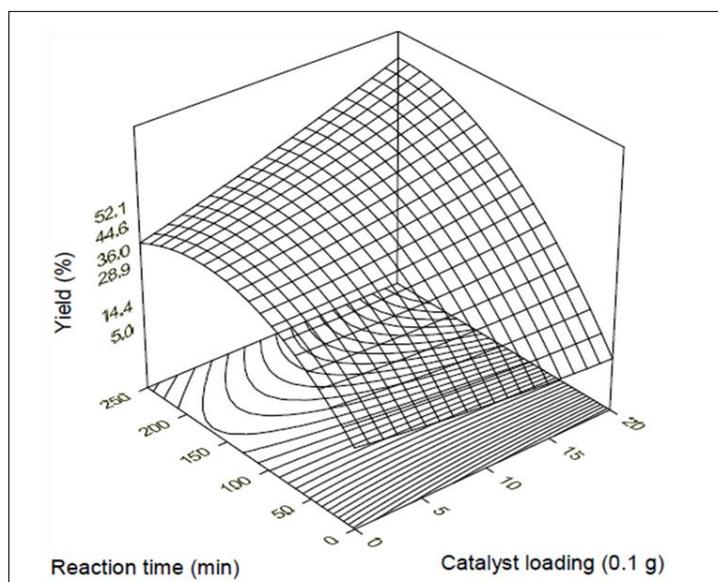

Fig. 4. 3D response surface plot of levulinic acid yield versus reaction time and catalyst loading

The effects of variables were further plotted for the interaction of reaction temperature and catalyst loading at 120 min of reaction time (Fig. 5).
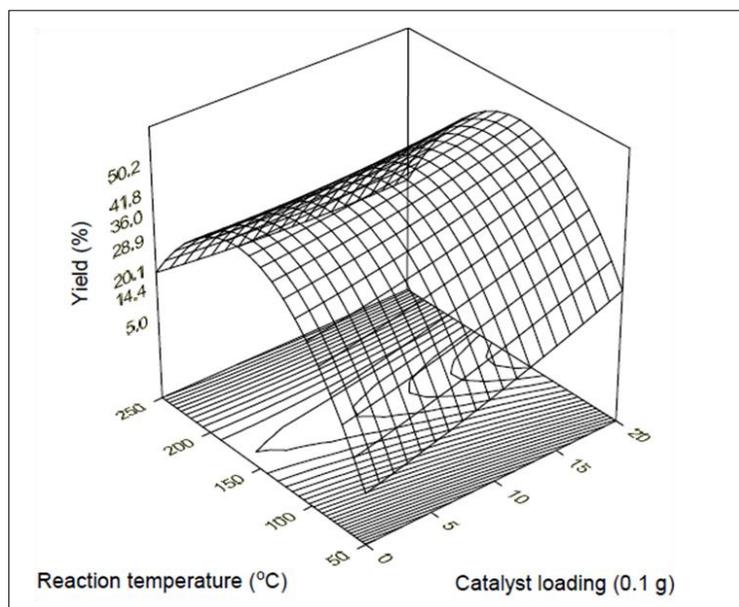

Fig. 5. 3D response surface plot of levulinic acid yield versus reaction temperature and catalyst loading

High levulinic acid yield could be obtained at medium reaction temperature. Meanwhile, a small amount of levulinic acid was produced at low reaction temperature due to the incomplete decomposition of cellulose to form levulinic acid. High reaction temperature is required to decompose crystalline structures of cellulose into amorphous structures before it can be furthered converted into levulinic acid. The levulinic acid yield linearly increased with increasing catalyst loading. Higher catalyst loading possibly can increase the acidic condition in the reaction process. Thus, levulinic acid yield could be enhanced by the reaction of intermediate product (HMF) under more acidic conditions. However, further increase of catalyst dosage did not give positive effects on the enhancement of levulinic acid yield. In addition, higher catalyst loading might increase the viscosity of the mixture. As a result, the mass transfer resistance in the mixture increased and reduced the effect of mixing. This suggests that no more catalyst should be loaded once the amount of catalyst loading succinctly meets the requirement of the reaction.

Optimization

Based on the model in Eq. 2, the optimum conditions to predict high levulinic acid yield are tabulated in Table 4. Further analysis was performed at optimum conditions for the verification of the predicted levulinic acid yield. The levulinic acid yield for the observed value was 46.0%, indicating a 1.44% error between the observed and predicted (46.67%) values. The error was considered small, as the observed value was within the 5% significance level. These process conditions were more favourable and effectively produced high levulinic acid yield compared to previous studies (Hegner *et al.* 2010; Peng *et al.* 2010; Potvin *et al.* 2011), which reported high levulinic acid yield at a high reaction temperature and longer reaction time.

Table 4. Predicted Levulinic Acid Yield at Optimum Process Conditions

Factor	Observed minimum	Critical values	Observed maximum
Temperature, (ºC)	61.8	176.5	238.2
Time, (min)	14.2	140.0	225.8
Catalyst loading, (0.1 g)	0.1	8.8	15.9

Ionic Liquid Application

The application of ionic liquid in the production of levulinic acid has not been reported previously (Rackemann and Doherty 2011). Extensive studies have been conducted recently on the production HMF, the intermediate product of levulinic acid, via heterogeneous acid catalyst, and with ionic liquid (Li *et al.* 2009; Su *et al.* 2009; Tao *et al.* 2010; Tao *et al.* 2011a,b; Wang *et al.* 2011). High yields of HMF were produced from sugars under these catalytic systems, and small amounts of levulinic acid were reported. Based on the results discussed above, this method implied that the ionic liquid has double functions: it could dissolve the cellulose and at the same time it could provide an acidic medium to weaken the glycosidic bonds in the cellulose structure. This could promote the hydrolysis of cellulose into monosaccharides more effectively before it can be further converted into HMF and rehydrated to produce levulinic acid over the hybrid catalyst. The hybrid catalyst could be involved in the hydrolysis of cellulose, wherein the Lewis acid sites could also weaken the glycosidic bonds and reacted like protonic acid. Interestingly, the combination of ionic liquid and hybrid catalyst in the conversion of

cellulose exhibited higher yield of levulinic acid under sufficient process conditions. Nevertheless, for the study involving the same hybrid catalyst, higher levulinic acid yield was attained with glucose compound (Ya'aini *et al.* 2012). The complex structure of the hollocellulose makes it difficult to decompose into products, but extensive studies are still required in this research area since hollocellulose is the most abundant compound among the biomass resources.

Utilization of Biomass

The potential of EFB and kenaf to produce levulinic acid over the hybrid catalyst demonstrated that levulinic acid yields of 15.5% and 15.0% were produced from EFB and kenaf, respectively at the optimum conditions. A high yield of levulinic acid can be obtained from biomass feedstock with high C_6-sugars content (Girisuta *et al.* 2008). Based on the results, there was no significant difference in the yield between EFB and kenaf, although high levulinic acid yield was expected in EFB due to higher cellulose content (41.0%) compared to kenaf (32.0%). The results could be attributed to glucomannan structure associated with increasing cellulose content in EFB. Another possible reason is due to the decomposition of cellulose in the EFB sample into other compounds such as formic acid, humin, furan derivatives, glycolic acid, acetic acid, and lactic acid. There were also esters of levulinic acid, which were ethyl levulinate and methyl levulinate in the biomass samples (Yan *et al.* 2008). In future work, these compounds should be identified so that the variation of reaction pathways can be determined.

The results from the present study demonstrated that, under the optimum conditions, almost half of the cellulose contents were converted into levulinic acid via the hybrid catalyst. The maximum theoretical levulinic acid yields were reported as 64.5% and 71.5% obtained from hexose and cellulose, respectively (Chang *et al.* 2007). The impressive result implied that the hybrid catalyst can also catalyze the lignocellulosic biomass to produce high yield of levulinic acid. The hybrid catalyst with large surface area and strong acidity influenced the surface reaction rates and reactivity towards the desired product.

Next, levulinic acid production from EFB and kenaf were studied in the presence of [EMIM][Cl] ionic liquid under the same process conditions. Results revealed that higher levulinic acid yields were obtained from EFB (20.0%) and kenaf (17.0%) in presence of ionic liquid. It can be surmised that the ionic liquid had reduced the crystal-linity of the holocellulose in the biomass and provided more accessibility for the biomass to convert to levulinic acid over the hybrid catalyst.

The presence of ionic liquid significantly reduced the reaction temperature and shortened the reaction time in the hybrid catalytic system for the cellulose or holocellulose conversion into levulinic acid. Previous studies have proven that the ionic liquid only changes the lignocellulosic biomass structure and does not alter the compositions of biomass (Singh *et al.* 2009; Tan *et al.* 2011). Indeed, the presence of ionic liquid could disrupt the covalent linkages between the biomass structures, dissolve the holocellulose, and allow the holocellulose chains accessible to the chemical transformation to produce levulinic acid by using the hybrid catalyst. Based on the results, high levulinic acid yields were produced from the sample with a large amount of cellulose which is EFB. Therefore, the EFB sample was more suitable to be utilized for the levulinic acid production in comparison to the kenaf sample.

CONCLUSIONS

1. Experimental results on cellulose demonstrated that high levulinic acid yield can be produced at the optimum process conditions over a hybrid (1:1) $CrCl_3$-HY zeolite catalyst.

2. Process variables such as reaction temperature, reaction time, and catalyst loading influenced levulinic acid yield.

3. The linear main effect of reaction time and quadratic main effect of reaction temperature significantly affected levulinic acid yield from cellulose.

4. At optimum conditions, 46.0% of levulinic acid yields were attained from cellulose. Utilization of EFB and kenaf at optimum conditions produced 15.5% and 15.0% of levulinic acid yield. Meanwhile, in the presence of ionic liquid, higher levulinic acid yields at 20.0% and 17.0% were obtained for EFB and kenaf samples, respectively.

5. Ionic liquid disrupted the covalent linkages between the biomass structures, dissolved the holocellulose, and allowed the holocellulose chains accessible to the chemical transformation to produce levulinic acid by using the hybrid catalyst.

6. High levulinic acid yield could be obtained from samples with large holocellulose content. Therefore, EFB is judged to be more suitable to be utilized for the levulinic acid production instead of kenaf.

ACKNOWLEDGMENTS

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