Optimization of Oil Palm Fronds Conversion to Levulinic Acid using Fe/HY Zeolite Catalyst

(Pengoptimuman Penukaran Pelepah Kelapa Sawit kepada Asid Levulinik menggunakan Pemangkin Fe/HY Zeolit)

NUR AAINAA SYAHIRAH RAMLI & NOR AISHAH SAIDINA AMIN*

ABSTRACT

Levulinic acid (LA) is a versatile platform chemical with numerous potential uses. Conversion of oil palm fronds (OPF) to LA over Fe/HY zeolite catalyst has been conducted in this study. The optimization process using Box-Behnken design gave 19.6% of LA yield at 181.7°C reaction temperature, 7.7 h reaction time, 1.13 g Fe/HY zeolite loading and 0.25 g OPF loading. The efficiency of OPF conversion at the optimum conditions was determined to be 61.1%. It was also demonstrated that Fe/HY zeolite gave sufficient performance for five successive cycles of OPF conversion to LA. The results suggested that Fe/HY zeolite is potential as catalyst for biomass conversion to LA.

Keywords: Fe/HY zeolite; levulinic acid; oil palm fronds; optimization

ABSTRAK

Asid levulinik (LA) merupakan bahan kimia serbaguna dengan pelbagai potensi penggunaan. Penukaran pelepah kelapa sawit (OPF) kepada LA menggunakan pemangkin Fe/HY zeolit telah dijalankan di dalam kajian ini. Proses pengoptimuman menggunakan reka bentuk Box-Behnken memberikan hasil LA sebanyak 19.6% pada suhu tindak balas 173.4°C, masa tindak balas 3.3 h, suapan Fe/HY zeolite 1.13 g dan suapan OPF 0.25 g. Kecekapan penukaran OPF pada keadaan optima ialah 61.1%. Ia juga menunjukkan bahawa Fe/HY zeolit memberikan prestasi yang mencukupi untuk lima kitaran berturutan bagi penukaran OPF kepada LA. Keputusan menunjukkan bahawa Fe/HY zeolite berpotensi sebagai pemangkin bagi penukaran biojisim kepada LA.

Kata kunci: Asid levulinik; Fe/HY zeolite; pelepah kelapa sawit; pengoptimuman

INTRODUCTION

Due to the depleting petroleum resources, researchers have embarked on the development of new technologies for the utilization of renewable biomass feedstocks for fuels and chemicals productions (Rackemann & Doherty 2011). Levulinic acid (LA) is a promising platform chemical, which can be produced from biomass conversion and can be converted to energy and carbon based products. Several studies have reported the LA production including acid-catalyzed dehydration of carbohydrate and hydrolysis of lignocellulosic biomass (Chang et al. 2007; Rackemann & Doherty 2011).

Heterogeneous catalysts have fascinated substantial interests since these types of catalyst can overcome the disadvantages associated with mineral acids in acid catalysis reaction. Previously, zeolite has been tested as catalysts for LA production (Jow et al. 1987; Liu et al. 2012; Lourvanij & Rorrer 1993; Zeng et al. 2010). Besides, metal salts can convert carbohydrates effectively into LA, with $CrCl_2$ or $CrCl_3$ were mostly used (Hu et al. 2011; Peng et al. 2010; Tan et al. 2011; Yuan et al. 2011). However, high price and toxicity of $CrCl_2$ and $CrCl_3$ have necessitated the search for a non- toxic and low cost catalyst. Due to

the low cost and non-toxic properties of $FeCl_3$ (Mao et al. 2013), it is envisaged that this extensively available compound is able to perform as an eco-friendly catalyst for LA production. However, by using zeolite and metal halide alone as catalyst, low LA yield has been reported in literatures (Peng et al. 2010; Tao et al. 2010; Zhang & Zhao 2009). Thus, modification of porous zeolite with acidic metal halide might improve the catalytic properties and enhance the LA production.

Optimization process is important as the optimize process conditions can increase the process efficiency, improve the product yield and reduce the capital or operating cost. Response surface methodology (RSM) is coped by certain regulations where the relationship between the variables can be used to optimize a desired output. RSM has been employed to optimize the production of LA from various feedstocks (Chang et al. 2007; Kang et al. 2013; Ya'aini et al. 2012).

In our previous study, Fe/HY zeolite catalyst has been tested for glucose conversion to LA (Ramli & Amin 2015). As glucose is the model compound of cellulose, where cellulose is the major constituents of biomass, herein Fe/HY zeolite was used as catalyst for OPF conversion to LA.

The aim of this study was to optimize LA production from OPF over Fe/HY zeolite catalyst using Box Behnken design under RSM. The variation of reaction process conditions (temperature, time, Fe/HY zeolite loading and OPF loading) which could affect the response (LA yield) were evaluated within the proposed range. Finally, the leaching of Fe ions from Fe/HY zeolite catalyst and the reusability of Fe/HY zeolite catalyst were also tested.

MATERIALS AND METHODS

MATERIALS

Iron (III) chloride (FeCl$_3$); 98%, ammonium chloride (NH$_4$Cl); 99%, and LA; 98% were purchased from Merck, Germany. NaY zeolite (SiO$_2$/Al$_2$O$_3$ = 5) was supplied by Zeolyst International. Sulfuric acid (H$_2$SO$_4$); 96% was obtained from Qrec, New Zealand. OPF was supplied by Malaysia Palm Oil Board (MPOB), Kuala Lumpur, Malaysia. The OPF samples were dried and grinded to small size particles (less than 5.0 mm).

Fe/HY ZEOLITE PREPARATION AND CHARACTERIZATION

The Fe/HY zeolite was prepared using wetness impregnation method, with 10% weight ratio of FeCl$_3$ to the HY zeolite (Ramli & Amin 2015). Fe/HY zeolite and parent HY zeolite were characterized using several methods. The FTIR spectra were recorded using Perkin Elmer in the range of 400-4000 cm^{-1}. The crystallinity of Fe/HY zeolite catalyst was analyzed by XRD employing Bruker D8 Advance diffractometer system. FESEM images of the catalysts were acquired to evaluate the morphology of the catalyst (Hitachi SU8020). N$_2$ physisorption method was applied to determine the surface area and pore volume using a Micromeritics ASAP2020 analyzer. The acidity of the catalyst was determined using temperature programmed desorption of ammonia (NH$_3$ –TPD, TPDRO 1100 series, Thermo Finnigin).

OPF CHARACTERIZATION

The compositions of OPF were determined by thermal gravimetric analysis (TGA) using a NETZSCH STA 449F3 instrument (Ramli & Amin 2014). The characterization of cellulose and hemicellulose content in OPF were in accordance with the standard laboratory analytical procedures provided by the National Renewable Energy Laboratory (Ramli & Amin 2014).

EXPERIMENTAL DETAILS

OPF hydrolysis was carried out by mixing OPF and Fe/HY zeolite catalyst at various amounts in 50 mL distilled water. The solution was heated up in a 100 mL high pressure reactor at the desired temperature with stirring speed, 200 rpm. The time required to reach the desired temperature was around 20 min. After the reaction was completed, the reaction mixture was cooled down to room temperature. The concentration of LA in the liquid product was determined by using HPLC (Perkin Elmer), Hi Plex H column, flow rate of 0.6 mL/min, 5 mM H$_2$SO$_4$ as mobile phase, UV 210 nm detector, 20 min retention time and column temperature of 60°C. The yield and theoretical yield of LA and efficiency of the process were calculated according to (1) - (3):

$$\text{LA yield (\%)} = \frac{\text{LA amount}}{\text{Initial OPF amount}} \times 100\%. \quad (1)$$

$$\text{Theoretical LA yield (\%)} = \frac{\text{Cellulose content} \times 0.71}{\text{Initial biomass amount}} \times 100. \quad (2)$$

$$\text{Efficiency (\%)} = \frac{\text{LA yield}}{\text{Theoretical LA yield}} \times 100\%. \quad (3)$$

EXPERIMENTAL DESIGN

Box-Behnken design (BBD) was used to design the experiment with four variables. The effect of reaction temperature (x_1), reaction time (x_2), Fe/HY zeolite loading (x_3) and OPF loading (x_4), were investigated at three different levels; low, medium, high (Table 1). This design was performed using Statsoft Statistica 8.0 software.

RESULTS AND DISCUSSION

Fe/HY ZEOLITE PROPERTIES

The Fe/HY zeolite and HY zeolite catalysts were characterized using several methods in order to inspect the physico-chemical properties of the catalysts (Ramli & Amin 2015). The prominent features are given in Table 2.

TABLE 1. Experimental range and levels for the independent variables

Factors	Symbol	Range and level		
	Coded	-1	0	+1
Reaction temperature (°C)	x_1	140	170	200
Reaction time (h)	x_2	4	6	8
Fe/HY zeolite loading (g)	x_3	0.5	1	1.5
OPF loading (g)	x_4	0.5	1	1.5

TABLE 2. Characteristics of Fe/HY zeolite catalyst

Method	Observation	Comment
FTIR	• 1,300-400 cm^{-1} indicated the framework vibration of lattice cell • 4000-3,000 cm^{-1} attributed to the hydroxyl groups attached to the zeolite structure • No significant band position shift for Fe/HY zeolite	Impregnation of Fe did not significantly affect the zeolite structure
FESEM-EDX	• Uniformly distributed small crystallites • Morphology of catalysts did not change significantly with Fe impregnation • EDX result of Fe species has confirmed the impregnation of 10% FeCl$_3$	No significant crystalline transformation occurred
XRD	• Peaks at 2θ; 6.35°, 23.7° and 15.8° assigned to the FAU structure • XRD pattern of Fe/HY matched with HY zeolite	Impregnation of Fe did not significantly affect the zeolite structure
BET	• Surface area of HY zeolite; 829.5 m^2/g and Fe/HY zeolite; 549.3 m^2/g • Pore volume of HY zeolite; 0.37 cm^3/g and Fe/HY zeolite; 0.27 cm^3/g	Surface area and pore volume of Fe/HY were smaller than HY zeolite catalyst due to the existence of larger constituents inside the pores
NH$_3$-TPD	• Acid site density of HY zeolite; 4.27 mmol/cm^3 and Fe/HY zeoliye 9.93 mmol/cm^3	The increase in acidity of Fe/HY is attributed to the presence of Fe species (Lee et al. 2009).

MODEL ANALYSIS

The experimental design according to BBD with 27 batch experiments and the respective LA yield are given in Table 2. The LA yield (Y_1) was the response for the tested variables; reaction temperature (x_1), reaction time (x_2), Fe/HY zeolite loading (x_3) and OPF loading (x_4). The second order polynomial model for LA yield is as in (4):

$$Y = -175.917 + 1.4067x_1 + 10.692x_2 + 26.373x_3 + 46.15x_4 - 0.0026x_1^2 - 0.21x_2^2 - 4.312x_3^2 - 4.122x_4^2 - 0.036x_1x_2 - 0.099x_1x_3 - 0.14x_1x_4 + 0.172x_2x_3 - 2.137x_2x_4 + 0.16x_3x_4$$

$$(4)$$

The model indicated the adequacy between the observed and predicted LA yield where the coefficient of determination (R^2) was close to 1. The values of R^2 for OPF conversion to LA was 0.9771. The results indicated that 97.71% of the variability in the response can be explained by the model. The high value of R^2 indicates that the model obtained is able to give a good estimate of the response within the process conditions range. Table 2 also exhibits the comparison between the predicted and the observed values of LA yield. The results indicated that a sufficient correlation between these values was observed. From Table 3, the analysis of variance (ANOVA) was used to check the model adequacy by comparing the calculated F-value with the tabulated F-value. In general, the calculated F-value should be greater than the tabulated F-value to reject the null hypothesis. The tabulated F-value was used at a high confidence level (95%) in order to obtain a good prediction model.

The significance of each coefficient was determined by t-value and p-value as shown in Pareto chart (Figure 1), where the values were used to understand the interactions between the variables. The greater the magnitude of the t-value and the smaller the p-value, the more significant was the corresponding coefficient (Chang et al. 2007; Wan Omar & Saidina Amin 2011). As illustrated in Figure 1, with smaller p-value and larger t-value, the quadratic term of all variables; reaction temperature (x_1^2), reaction time (x_2^2), Fe/HY zeolite loading (x_3^2) and OPF loading (x_4^2) gave a remarkable effect on the LA yield. This suggests that increasing each individual parameter will increase the LA yield until it reached its optimum value. Besides, there is also interaction of linear term for reaction temperature and time (x_1x_2), reaction temperature and OPF loading (x_1x_4), reaction time and OPF loading (x_2x_4) and reaction temperature and Fe/HY zeolite loading (x_1x_3). Most of the significant coefficients are convincing at 99% significant level, while some are significant at 95%. With p-value higher than 0.05, it is confirmed that there is less interaction between reaction time and Fe/HY zeolite loading (x_2x_3) and Fe/HY zeolite loading and OPF loading (x_3x_4), on LA yield from OPF.

VARIABLES EFFECT ON LA YIELD

The response surface plots and contour plots are presented in Figure 2. The plots were used to explain the interaction between two variables and the response. The surface confined in the smallest ellipse in the contour plot indicates the optimum value of the variables at maximum predicted value of the response (Chang et al. 2007).

The interaction of reaction temperature with reaction time, Fe/HY zeolite loading, and OPF loading, respectively,

TABLE 3. Experimental design for OPF conversion to LA

Run	Variables				Response	
	x_1	x_2	x_3	x_4	LA yield, Y_1 (%)	
	(°C)	(h)	(h)	(g)	Experimental	Predicted
1	140.0	4.0	1.0	1.0	11.8	12.2
2	140.0	8.0	1.0	1.0	17.3	16.9
3	200.0	4.0	1.0	1.0	20.5	20.7
4	200.0	8.0	1.0	1.0	17.4	16.7
5	170.0	6.0	0.5	0.5	16.2	16.0
6	170.0	6.0	0.5	1.5	17.2	17.3
7	170.0	6.0	1.5	0.5	18.4	18.0
8	170.0	6.0	1.5	1.5	19.5	19.4
9	140.0	6.0	1.0	0.5	11.0	11.6
10	140.0	6.0	1.0	1.5	17.0	17.2
11	200.0	6.0	1.0	0.5	20.0	19.9
12	200.0	6.0	1.0	1.5	17.6	17.0
13	170.0	4.0	0.5	1.0	17.4	16.8
14	170.0	4.0	1.5	1.0	18.9	18.5
15	170.0	8.0	0.5	1.0	16.4	17.0
16	170.0	8.0	1.5	1.0	18.6	19.5
17	140.0	6.0	0.5	1.0	12.2	11.2
18	140.0	6.0	1.5	1.0	17.4	16.8
19	200.0	6.0	0.5	1.0	18.3	19.1
20	200.0	6.0	1.5	1.0	17.6	18.0
21	170.0	4.0	1.0	0.5	14.9	15.4
22	170.0	4.0	1.0	1.5	20.3	20.5
23	170.0	8.0	1.0	0.5	19.8	19.6
24	170.0	8.0	1.0	1.5	16.7	16.6
25	170.0	6.0	1.0	1.0	19.9	19.8
26	170.0	6.0	1.0	1.0	19.5	19.8
27	170.0	6.0	1.0	1.0	20.0	19.8

TABLE 4. Analysis of variance (ANOVA) for quadratic model of OPF conversion to LA

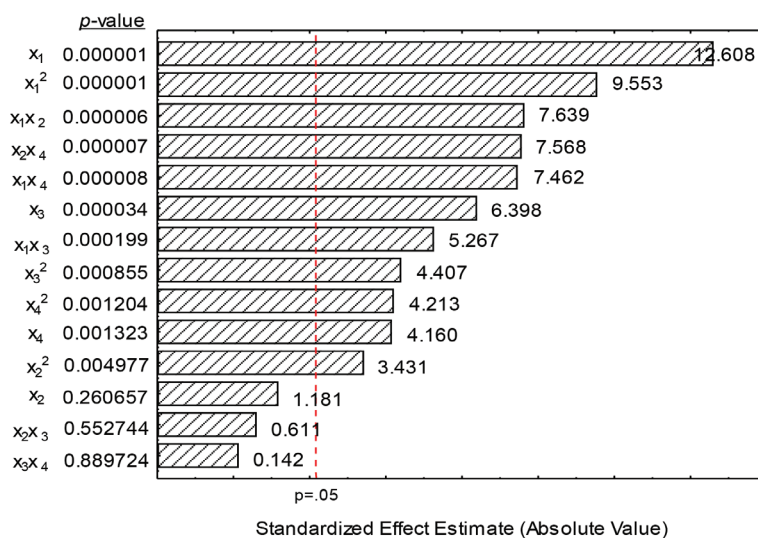| Sources	Sums of square	Degree of freedom	Mean square	F-value	$F_{0.05,14,12}$
Regression	163.25	14	11.66	36.44	2.64
Residual	3.84	12	0.32		
Total	167.09	26			

FIGURE 1. Pareto chart of OPF conversion to LA

were observed on LA yield (Figures 2(a)-2(c)). The interaction effects between reaction temperature and time on LA yield in Figure 2(a) shows that LA yield linearly increased with increasing reaction temperature and time up to the optimum conditions. At low temperature, prolonged reaction time allowed the cellulose in the OPF to be dissolved and to be converted into LA. It is known that elevated temperature can cause the acceleration of reaction rate (Chang et al. 2007; Fang & Hanna 2002). However, the unwanted carbonaceous residue was also produced at higher temperature, prolonged reaction time, higher feedstock and catalyst loading, deducing side reactions increased at the same time. The same trend also has been observed previously (Peng et al. 2010).

As an important variable, increasing the Fe/HY zeolite loading favor the LA production, due to the higher number of reactive sites in the reaction system (Figure 2(b)). After the Fe/HY zeolite loading met the optimum requirement, higher temperature resulted in lower LA yield. Higher catalyst loading might decrease the LA yield, probably due to the side reactions and accumulation of byproducts. In this process, hydrolysis of OPF can result in a variety of products such as 5-hydroxymethylfurfural (5-HMF), formic acid, furfural and LA as the main product. As shown in Figure 2(c), when the OPF loading increased, higher temperature is needed to dissolve the OPF then increase the LA yield, as a consequence of limited active sites in the reaction system. Besides, higher OPF loading would increase the probability of the reactive compounds generated from OPF such as sugars and 5-HMF, collided with each other and caused cross polymerization to produce undesired products.

Figure 3(d) and 3(e) exhibit the interaction of reaction time with OPF and Fe/HY zeolite loading, respectively. The LA yield increases with longer reaction time at lower OPF and Fe/HY loading. With limited amount of acid catalyst, prolonged reaction time was needed for the conversion of OPF to LA. The same trend has also been reported previously for homogeneous acid catalyst (Cha & Hanna 2002; Kang et al. 2013). Lower LA yield at higher catalyst loading and prolonged reaction time was due to the excess active sites of the catalyst and increase of the undesired by-products. At 170°C and 6 h reaction conditions, the circular nature of the contour plot (Figure 3(f)) can be observed, which indicates less significant effects of interaction between OPF and Fe/HY loading on the LA yield. The LA yield increases to the maximum and then start to decrease after overloading the OPF and Fe/HY zeolite in the reaction system. The excess numbers of OPF and Fe/HY zeolite loading might resulted in side reactions and accumulation of by-products. Therefore, the determination of optimal reaction conditions for maximizing the LA production from OPF conversion is important for the process to be economically viable.

OPTIMIZATION OF LA YIELD

The response surface analysis predicted that the optimum LA yield from OPF was 20.1% at 181.7°C reaction temperature, 7.7 h reaction time, 1.13 g Fe/HY zeolite loading and 0.52 g OPF loading. Further analysis was performed for the verification of the predicted yield. The LA yield at the optimum conditions was 19.6% indicating a 2.5% error between the observed and predicted yield.

OPF were characterized using TGA and acid hydrolysis process (Ramli & Amin 2014). Few distinct stages of weight losses were observed from TGA, showing the moisture (12.8%), holocellulose (65.5), lignin (11.2%) and ash (10.5%) content in the OPF sample. The cellulose and hemicellulose contents in OPF were further analyzed using acid hydrolysis procedure. From the analysis, OPF contains 45.2 and 20.3% of cellulose and hemicellulose, respectively (Ramli & Amin 2014). The determination of cellulose content in OPF can be used to determine the highest theoretical yield of LA and to calculate the process efficiency. The theoretical LA yield from OPF with 45.2% cellulose content is 32.1%. The efficiency of OPF conversion to LA in this study has been accounted as 61.1%. It shows that more than half of the cellulose content in OPF was successfully converted into LA by using Fe/HY zeolite as catalyst. Higher efficiency was achieved in this study, compared to the previous study on LA production from biomass (Girisuta et al. 2008; Ya'aini et al. 2012). Generally, 100% efficiency of biomass conversion to LA is not achievable. This is attributed to other possible parallel reactions that could have occurred in the system including fragmentation and polymerization reactions (Zeng et al. 2010). Besides, biomass recalcitrant has caused difficulty for the hydrolysis process. Therefore, biomass pre-treatment such as superfine grinding and steam explosion method could enhance the hydrolysis process and increase the LA yield (Chen et al. 2011).

A reaction pathway for the production of LA from OPF is shown in Figure 3 in order to give a better insight of the process. The dissolution of OPF structure was first takes place followed by the hydrolysis of cellulose to give glucose. Then, glucose was dehydrated to 5-HMF, the intermediate product of LA. Finally, 5-HMF was rehydrated to LA.

REUSABILITY OF Fe/HY ZEOLITE

The reusability of heterogeneous catalyst is one of the main advantages over homogeneous catalyst. In this study, the reusability of Fe/HY zeolite has been tested for the conversion of OPF to LA, at 180°C for 8 h, using 1.1 g Fe/HY and 0.5 g OPF (for the first cycle). After each cycle, Fe/HY zeolite was recovered by centrifugation, washed, dried overnight and calcined before returned to the subsequent cycles. For the subsequent cycles, the reaction was conducted at 180°C for 8 h, using 0.5 g OPF and the remaining catalyst from the previous cycle. The Fe/HY zeolite could be reused up to five times with the decrement of LA yield less than 6% (Figure 4), probably due to the decrease in catalyst amount as a consequence of the multiple filtration and washing steps. Besides, the presence of remaining OPF ash in the solid residue
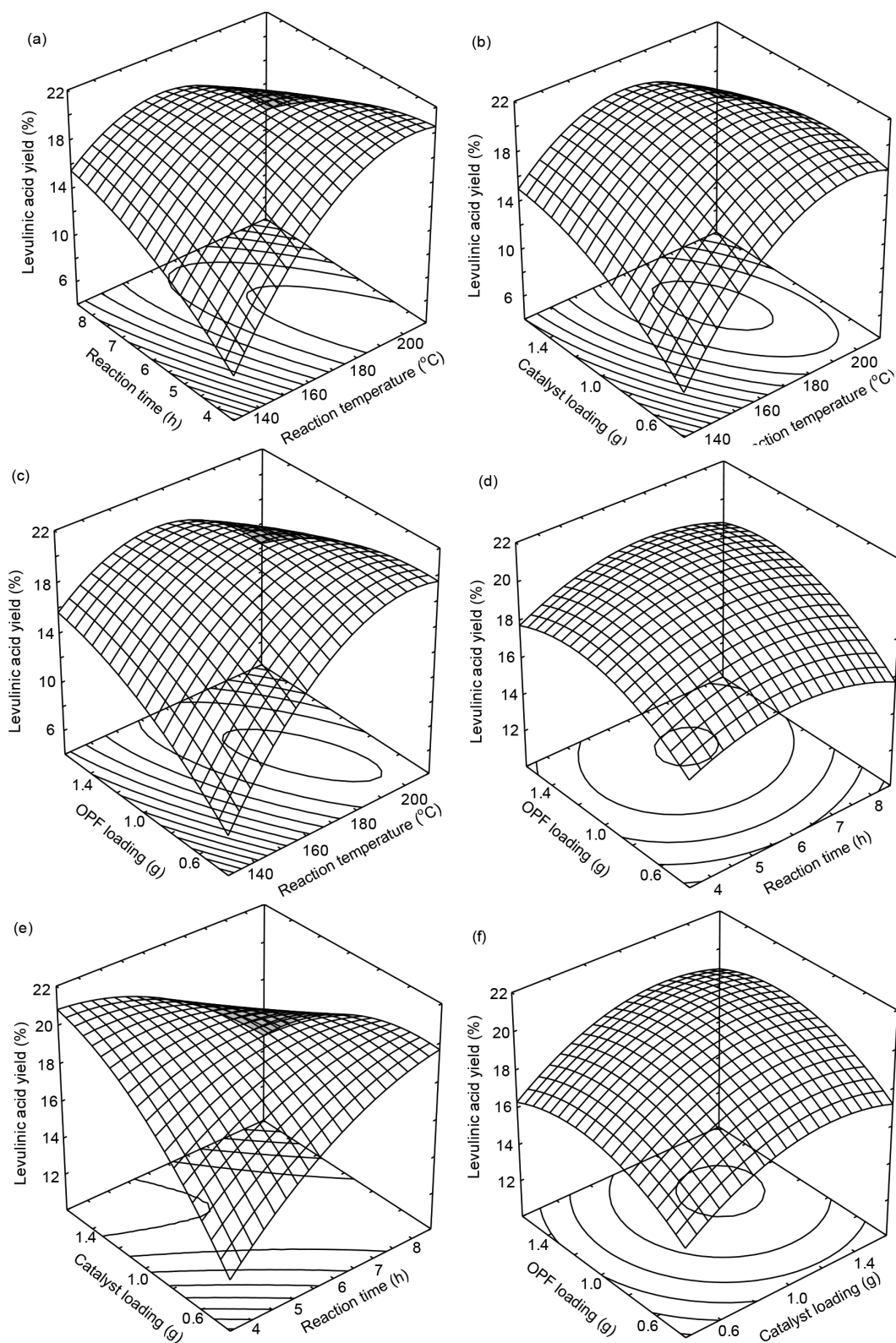
FIGURE 2. Response surface plots of LA yield versus different variables

could reduce the catalyst activity in the subsequent runs. The possible leaching of Fe from the Fe/HY zeolite into the solution was studied using atomic absorption spectroscopy. The amount of Fe ions was found to be less than 1% of the starting Fe, suggesting that the hydrolysis reaction was mostly due to presence of Fe on the Fe/HY zeolite surface rather than trace amount of leached Fe ions.
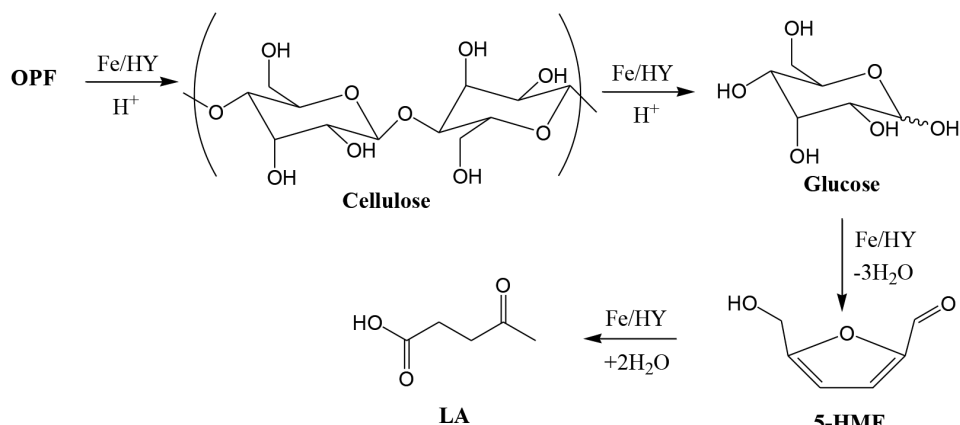
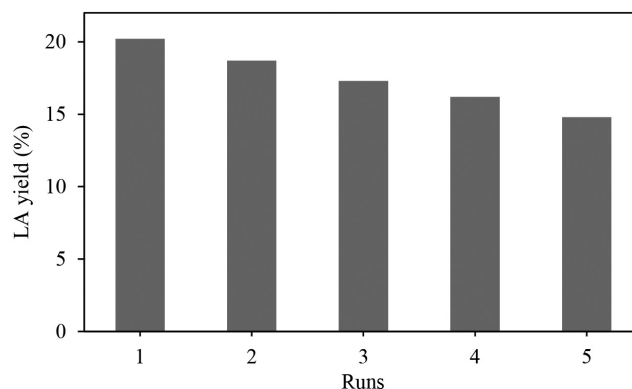FIGURE 3. Reaction pathway of LA production from OPF

FIGURE 4. Reusability of Fe/HY zeolite for OPF conversion to LA

CONCLUSION

Based on the experimental results, it can be concluded Fe/HY zeolite could act as an effective solid catalyst for the production of LA from OPF. Four reaction parameters including reaction temperature, reaction time, Fe/HY zeolite loading and OPF loading were optimized using RSM. At optimum conditions (181.7°C reaction temperature, 7.7 h reaction time, 1.13 g Fe/HY zeolite loading and 0.52 g OPF loading), 19.6% LA yield was obtained from OPF with 61% efficiency. The results showed that Fe/HY zeolite worked effectively as a reusable catalyst for OPF conversion to LA.

REFERENCES

Cha, J.Y. & Hanna, M.A. 2002. Levulinic acid production based on extrusion and pressurized batch reaction. *Industrial Crops and Products* 16(2): 109-118.

Chang, C., Cen, P. & Ma, X. 2007. Levulinic acid production from wheat straw. *Bioresource Technology* 98(7): 1448-1453.

Chen, H., Yu, B. & Jin, S. 2011. Production of levulinic acid from steam exploded rice straw via solid superacid. *Bioresource Technology* 102(3): 3568-3570.

Fang, Q. & Hanna, M.A. 2002. Experimental studies for levulinic acid production from whole kernel grain sorghum. *Bioresource Technology* 81(3): 187-192.

Girisuta, B., Danon, B., Manurung, R., Janssen, L.P.B.M. & Heeres, H.J. 2008. Experimental and kinetic modelling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid. *Bioresource Technology* 99(17): 8367-8375.

Hu, L., Sun, Y. & Lin, L. 2011. Efficient conversion of glucose into 5-Hydroxymethylfurfural by chromium(III) chloride in inexpensive ionic liquid. *Industrial & Engineering Chemistry Research* 51(3): 1099-1104.

Jow, J., Rorrer, G.L., Hawley, M.C. & Lamport, D.T.A. 1987. Dehydration of d-fructose to levulinic acid over LZY zeolite catalyst. *Biomass* 14(3): 185-194.

Kang, M., Kim, S.W., Kim, J.W., Kim, T.H. & Kim, J.S. 2013. Optimization of levulinic acid production from Gelidium amansii. *Renewable Energy* 54(0): 173-179.

Lee, S.K., Jang, Y.N., Bae, I.K., Chae, S.C., Ryu, K.W. & Kim, J.K. 2009. Adsorption of toxic gases on iron-incorporated

Na-A zeolites synthesized from melting slag. *Materials Transactions* 50(10): 2476-2483.

Liu, Y., Lin, L., Sui, X.Y., Zhuang, J.P. & Pang, C.S. 2012. Characterization of ZSM-5 during conversion of glucose to levulinic acid. *Applied Mechanics and Materials* 260-261: 1206-1209.

Lourvanij, K. & Rorer, G.L. 1993. Reactions of aqueous glucose solutions over solid-acid Y-zeolite catalyst at 110-160 .degree.C. *Industrial & Engineering Chemistry Research* 32(1): 11-19.

Mao, L., Zhang, L., Gao, N. & Li, A. 2013. Seawater-based furfural production via corncob hydrolysis catalyzed by FeCl3 in acetic acid steam. [10.1039/C2GC36346A]. *Green Chemistry* 15(3): 727-737.

Peng, L., Lin, L., Zhang, J., Zhuang, J., Zhang, B. & Gong, Y. 2010. Catalytic conversion of cellulose to levulinic acid by metal chlorides. *Molecules* 15(8): 5258-5272.

Rackemann, D.W. & Doherty, W.O.S. 2011. The conversion of lignocellulosics to levulinic acid. *Biofuels, Bioproducts and Biorefining* 5(2): 198-214.

Ramli, N.A.S. & Amin, N.A.S. 2015. Fe/HY zeolite as an effective catalyst for levulinic acid production from glucose: Characterization and catalytic performance. *Applied Catalysis B: Environmental* 163(0): 487-498.

Ramli, N.A.S. & Amin, N.A.S. 2014. Catalytic hydrolysis of cellulose and oil palm biomass in ionic liquid to reducing sugar for levulinic acid production. *Fuel Processing Technology* 128(0): 490-498.

Tan, M., Zhao, L. & Zhang, Y. 2011. Production of 5-hydroxymethyl furfural from cellulose in CrCl2/Zeolite/BMIMCl system. *Biomass and Bioenergy* 35(3): 1367-1370.

Tao, F., Song, H. & Chou, L. 2010. Hydrolysis of cellulose by using catalytic amounts of FeCl2 in ionic liquids. *ChemSusChem* 3(11): 1298-1303.

Wan Omar, W.N.N. & Saidina Amin, N.A. 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass and Bioenergy* 35(3): 1329-1338.

Ya'aini, N., Amin, N.A.S. & Asmadi, M. 2012. Optimization of levulinic acid from lignocellulosic biomass using a new hybrid catalyst. *Bioresource Technology* 116(0): 58-65.

Yuan, Z., Xu, C., Cheng, S. & Leitch, M. 2011. Catalytic conversion of glucose to 5-hydroxymethyl furfural using inexpensive co-catalysts and solvents. *Carbohydrate Research* 346(13): 2019-2023.

Zeng, W., Cheng, D.G., Zhang, H., Chen, F. & Zhan, X. 2010. Dehydration of glucose to levulinic acid over MFI-type zeolite in subcritical water at moderate conditions. *Reaction Kinetics, Mechanisms and Catalysis* 100(2): 377-384.

Zhang, Z. & Zhao, Z.K. 2009. Solid acid and microwave-assisted hydrolysis of cellulose in ionic liquid. *Carbohydrate Research* 344(15): 2069-2072.

Chemical Reaction Engineering Group (CREG)
Faculty of Chemical Engineering
Universiti Teknologi Malaysia
81310 UTM Skudai, Johor Darul Takzim
Malaysia

*Corresponding author; email: noraishah@cheme.utm.my