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RESEARCH ARTICLE

Optimizing levulinic acid from cellulose catalyzed by HY-zeolite immobilized ionic liquid (HY-IL) using response surface methodology

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Abstract

Levulinic acid (LA) is an ideal platform chemical with various applications. Ionic liquid,1,4-methyl sulfonic acid imidazolium tetrachloroaluminate ([MSIM][AlCl4]) has been immobilized into HY zeolite and tested for the conversion of cellulose to LA. Response surface methodology (RSM), based on Box–Behnken design (BBD), was employed to identify the optimum conditions for LA production. Experimental results indicate that the second-order model was sufficient for all independent variables with $R^2 = 0.90$. The optimum temperature, reaction time, catalyst dosage, and feedstock loading for cellulose conversion are 200 °C, 7 h, 0.6 g, and 0.3 g, respectively with LA yield of 27.2%. Meanwhile, the LA yield from oil palm frond (OPF) and empty fruit bunch (EFB) at the optimum condition is 24.1% and 21.3%, respectively. The efficiency of OPF and EFB for LA production is 75% and 72%, respectively. This study demonstrates the potential of HY-IL for biomass conversion to levulinic acid under mild condition.

Keywords: Levulinic acid, cellulose, optimization, zeolite, ionic liquid

INTRODUCTION

Research on lignocellulosic biomass for producing fuel and chemicals has increased due to its abundance, renewability, and worldwide distribution [1]. Oil palm frond (OPF) and empty fruit bunch (EFB) are among the several lignocellulosic biomass wastes that are available in Malaysia [2, 3]. Both OPF and EFB contain high amount of cellulose (23-65.0% for EFB and 41.7-62.3% for OPF) and have the potential to produce chemical and fuel [4-6].

Among the chemicals that have received great interest from researchers is levulinic acid (LA) due to its versatility as a platform chemical for fuel additives, polymer, solvent, food additives, pharmaceutical agents, and other bio-based chemicals [7]. Generally, there are several steps to produce LA from cellulose. First, the cellulose is hydrolyzed to glucose, followed by dehydrating the glucose to 5-hydroxymethylfurfural (5-HMF), and subsequently rehydrating the 5-HMF to form LA and formic acid [8].

In previous works, homogeneous catalysts such as phosphotungstic acid [9], sulfuric acid [10, 11], hydrochloric acid [12], and ionic liquid (IL) [13] are often used for production of LA. Among homogeneous catalysts used for LA production, ILs has received great attention in biomass research for producing chemicals. This is due to the advantages offered by ILs such as low vapor pressure, low melting point, and high thermal stability [14]. The properties of ILs can be tuned by changing their cation and anion [15]. Several ILs have been used as catalysts in LA production. Tao et al. applied ionic liquid 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate for LA production from cellulose in the presence of cobalt sulfate ($CoSO_4$) [16]. Huifang et al. demonstrated that SO_3H-functionalized ionic liquids effectively catalyze the conversion of cellulose to LA under microwave irradiation [17]. Despite their excellent activity in reaction, ILs as homogeneous catalyst present serious drawbacks such as high cost, equipment corrosion, and difficult to separate [18].

Therefore, heterogeneous catalysts have been introduced to overcome the problems associated with homogenous catalysts. H-type zeolite catalyst, a type of heterogeneous catalyst, has been frequently used for LA production due to its porosity, thermal stability, and high surface area [19, 20]. However, using H-type zeolite alone as catalyst for cellulose hydrolysis, low LA yield has been reported in previous work [21]. The reason for poor performance of zeolite catalyst was attributed to the low acid density of zeolite catalyst. Taking the advantage of IL's excellent activity for cellulose conversion, immobilizing IL into HY-zeolite might promote LA production from cellulose.

In this study, RSM was applied to obtain the optimum condition for LA production from cellulose catalyzed by HY-IL. The effects of the process variables; reaction temperature, reaction time, catalyst loading, and cellulose loading were investigated on production of LA. The significance of and the interaction between the process variables were also investigated using RSM. The predicted optimum condition was validated with the experimental values and tested on biomass samples OPF and EFB.

EXPERIMENTAL

Materials

The starting materials, microcrystalline cellulose was purchased from Sigma Aldrich. The OPF and EFB samples used in this study were collected from Malaysian Palm Oil Board (MPOB). HY zeolite (Si/Al ratio=30) was purchased from Zeolyst International, U.S.A. 1-Methylimidazole, chlorosulfonic acid (HSO_3Cl), and aluminium chloride ($AlCl_3$) were obtained from Merck, Germany. Dichloromethane (CH_2Cl_2) was obtained from QReC, New Zealand.

Analytical grade LA (Merck) was used for analysis of the product. The OPF and EFB samples used in this study were similar with the previous works [22, 23]. The approximate composition of OPF is 45.2% of cellulose, 20.3% of hemicellulose, 11.2% of lignin, 12.8% of moisture and 10.5% of ash content, while EFB has 41.0% of cellulose, 13.3% of hemicellulose, 25.2% of lignin, 10.6% of moisture content, and 8.0% ash content.

Preparation of HY-IL

The ionic liquids in this study were synthesized according to the method described in literature [24]. First, [MSIM][Cl] was prepared by adding HSO_3Cl dropwise to 1-methylimidazole in dry CH_2Cl_2 for 5 min in an ice bath and stirred for 2 h. After stirring, the CH_2Cl_2 was decanted and the resulting precipitate was washed with dry CH_2Cl_2 before being dried under vacuum to obtain [MSIM][Cl], a viscous pale yellow oil. For the synthesis of [MSIM][$AlCl_4$], equimolar $AlCl_3$ and [MSIM][Cl] were mixed for 5 min at 50 °C. The resulting mixture was then stirred for 1 h at 50 °C to give [MSIM][$AlCl_4$] as white powder.

HY-IL was synthesized according to the method described in literature [25]. HY zeolite was added to [MSIM][$AlCl_4$] solution in water with ionic liquid-to-zeolite weight ratio of 1:2. The mixture was stirred at 90 °C for 12 h. Finally, the catalyst was dried at 70 °C under vacuum to yield HY-IL.

Catalytic testing and analysis of product

All experiments were performed in a stainless-steel batch reactor using a certain amount of cellulose and catalyst. The reactor was preheated to the desired temperature. During the reaction, the stirrer was fixed at 200 rpm. The mixture then rapidly cooled down to room temperature. Similar tests were applied for utilization of OPF and EFB at the optimum condition. The concentration of LA was analyzed using high performance liquid chromatography (HPLC)(Agilent) equipped with Aminex HPX-87H column and UV detector. The HPLC was operated at 60 °C. The mobile phase used was 5mM sulfuric with flow rate of 0.6 mL/min. The LA yield for all experiment was computed as Eq. 1,

$$LA\ yield(\%) = \frac{LA\ amount\ (g)}{Initial\ feedstock\ amount\ (g)} \times 100 \qquad (1)$$

While for biomass experiment, theoretical LA yield and efficiency biomass were determined as follow;

$$Thereotical\ LA\ yield\ (\%) = \frac{cellulose\ \ amount\ (g) \times 0.71}{biomass\ \ amount\ (g)} \times 100 \qquad (2)$$

$$Efficiency(\%) = \frac{LA\ yield}{Thereotical\ LA\ yield} \times 100 \qquad (3)$$

where 0.71 is ratio of molecular weight of LA to molecular weight of cellulose. The efficiency refers to the efficiency of biomass conversion to LA based on cellulose content.

Experimental design

Three level four factor Box–Behnken design (BBD) using Statistica 8.0 was applied in this study (Table 1). Four variables including reaction temperature (A), reaction time (B), catalyst loading (C), and cellulose loading (D) were evaluated to investigate their effect on the LA production from cellulose.

Table 1 Coded and value for the independent variables.

Factors	Symbol	Range and level		
		−1	**0**	**+1**
Reaction temperature (°C)	A	160.0	180.0	200.0
Reaction time (h)	B	4.0	6.0	8.0
Catalyst loading (g)	C	0.2	0.4	0.6
Cellulose loading (g)	D	0.2	0.4	0.6

The general form second-order polynomial equation for LA yield was as follows:

$$Yi = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} x_i x_j \qquad (4)$$

where Y_i is predicted response (LA yield); x_i and x_j are the independent variables; βo is the model intercept; β_i, β_{ii} and βij are linear, quadratic and second-order interaction effect, respectively.

RESULTS AND DISCUSSION

RSM study for LA production from cellulose

The production of LA from cellulose was conducted in an aqueous solution. Cellulose was used as a model compound before applying lignocellulosic biomass for LA production.

To optimize the reaction condition and investigate the interaction between process variables for LA production, BBD statistical approach was employed. The results from the experiment design for LA production from cellulose are shown in Table 2. The estimated model for LA yield from cellulose using HY-IL is shown in Eq. 5.

$$Y = -253.912 + 2.587A - 5.475B - 101.375C + 179.292D - 0.007A^2 - 0.299B^2 - 98.021C^2 - 6.458D^2 + 0.059AB + 0.825AC - 0.888AD + 5.875BC - 6.563BD + 34.375CD \qquad (5)$$

The proposed model has the coefficient of determination (R^2) of 0.90 as shown in Fig. 1. This indicates that sample variation of 90% for LA yield is attributed to the process variables and the variation can be explained by the model. The high value of R^2 gives good estimate of the responses within the process condition range.

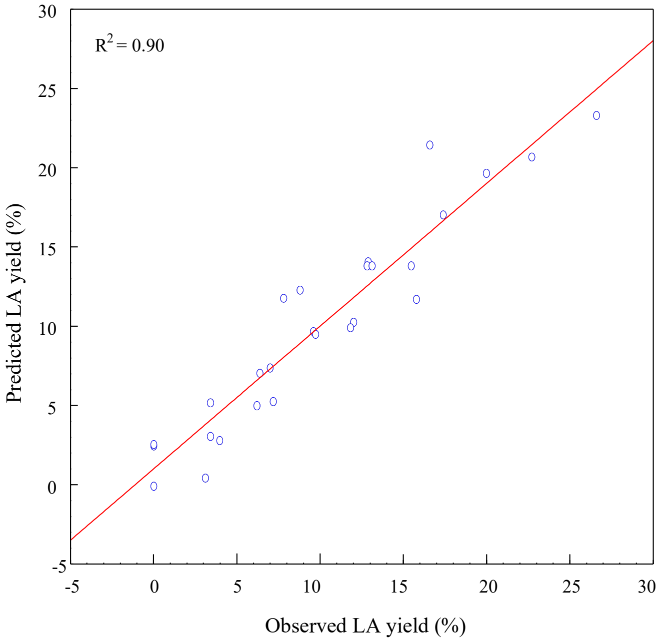

Fig. 1. The coefficient of determination of predicted versus observed value for LA yield.

The analysis of variance (ANOVA) for LA production from cellulose is presented in Table 3. The significance of each coefficient was determined by Student's *t* test and *p* values. The higher *t* value and smaller *p* value, the more significant the corresponding coefficient is. The *p* value smaller than 0.05 indicate the term is significant. As shown in Table 3, the linear terms *A*, *B,* and *C* were significant. For quadratic term, A^2 and C^2 were significant. For interaction term, *AD* was the most significant among them. The *p* values higher than 0.05 indicate that the terms *BC*, *BD* and *CD* are less significant on the LA yield from cellulose. Meanwhile, the lack of fit was not significant when the *p* value was more than 0.05. Therefore, it can be concluded that, the proposed model is significant and suitable for representing the data.

Table 2 Experimental design and result for LA yield from cellulose.

Run	Variables				Response
	A	*B*	*C*	*D*	Y_i
	Temperature (°C)	**Time (h)**	**Catalyst (g)**	**Cellulose (g)**	**LA yield (%)**
1	160.0	6.0	0.4	0.2	4.0
2	200.0	6.0	0.4	0.6	7.8
3	160.0	6.0	0.4	0.6	3.4
4	200.0	4.0	0.2	0.4	16.6
5	180.0	8.0	0.2	0.4	9.6
6	180.0	4.0	0.6	0.4	12.9
7	180.0	8.0	0.6	0.4	0.0
8	180.0	6.0	0.4	0.4	8.8
9	180.0	6.0	0.2	0.4	12.8
10	160.0	6.0	0.2	0.4	0.0
11	200.0	6.0	0.6	0.4	26.6
12	160.0	6.0	0.6	0.4	3.4
13	200.0	4.0	0.4	0.2	15.8
14	180.0	8.0	0.4	0.2	6.2
15	180.0	4.0	0.4	0.6	7.2
16	180.0	8.0	0.4	0.6	7.0
17	180.0	6.0	0.4	0.4	17.4
18	180.0	6.0	0.4	0.2	13.1
19	160.0	6.0	0.4	0.6	0.0
20	200.0	6.0	0.4	0.6	6.4
21	160.0	4.0	0.2	0.4	3.1
22	200.0	8.0	0.2	0.4	22.7
23	180.0	4.0	0.6	0.4	9.7
24	180.0	8.0	0.6	0.4	20.0
25	180.0	6.0	0.4	0.4	12.0
26	180.0	6.0	0.2	0.4	11.8
27	180.0	6.0	0.4	0.4	15.5

Variable effect on the responses

Fig. 2 depict 3D response surface plots for the LA yield, drawn by plotting LA yield versus two variables while maintaining other variable at fixed value. Fig. 2(a–c) show the relationship of reaction temperature with reaction time, catalyst loading, and feedstock loading, respectively. Small amount of LA was produced at low temperature due to incomplete decomposition of cellulose to LA. High reaction temperature is needed to change the crystal structure of cellulose to amorphous structure for further conversion of cellulose to LA. As shown in Fig. 2(a), LA yield increased with increasing reaction temperature due to the enhancement of the cellulose solubility, which increased the conversion rate of cellulose to LA. Fig. 2(b) shows the effects of reaction temperature and catalyst loading on LA yield. High catalyst loading and high reaction temperature favored LA yield. Increasing HY-IL loading provided more acidic sites in the reaction system and subsequently increased the LA yield. Fig. 2(c) illustrates the effect of reaction temperature and feedstock loading on LA yield. A higher feedstock loading reduced LA yield This could be due to insufficient active site on the catalyst for the conversion of cellulose.

Table 3 ANOVA of the proposed model.

Sources	Sum of squares	Degree of freedom	Mean square	*F* value	*p* value
Model	1128.32	14	80.59	7.75	0.000529
A	560.33	1	560.33	255.86	0.003886
B	73.50	1	73.51	33.56	0.028524
C	205.62	1	205.62	93.89	0.010483
D	14.64	1	14.65	6.68	0.122621
AB	22.09	1	22.09	10.086	0.086474
AC	43.56	1	43.56	19.89	0.046776
AD	50.41	1	50.41	23.01	0.040803
BC	22.09	1	22.09	10.08	0.086474
BD	27.56	1	27.56	12.58	0.071087
CD	7.56	1	7.56	3.45	0.204235
A^2	43.57	1	43.57	19.89	0.046762
B^2	7.62	1	7.63	3.48	0.203002
C^2	81.98	1	81.98	37.43	0.025686
D^2	0.35	1	0.36	0.16	0.725857
Residual	124.8	12	10.40		
Lack of fit	120.42	10	12.04	5.49	0.163583
Pure error	4.38	2	2.19		
Total	1253.12	26			

Fig. 2(d–e) demonstrate the relationship of reaction time with catalyst loading and cellulose loading, respectively. Prolonged reaction time with lower cellulose loading and higher catalyst loading could promote LA yield. For limited amount of acid catalyst, prolonged reaction time is needed to convert cellulose to LA. The same trend has been observed for homogenous acid catalyst [26].

Fig. 2(f) illustrates the effect of catalyst loading and cellulose loading on LA yield. High LA yield was obtained at medium catalyst loading. Excess catalyst loading could decrease LA yield. This condition possibly occurred due to unwanted side reaction. In addition, higher cellulose loading and catalyst loading could result in the increase of viscosity in the reaction mixture.

This results in increased mass transfer resistance and the effect of mixing is reduced. Consequently, less cellulose is available for the reaction. Thus, no more catalyst should be added when the amount of the catalyst has met the requirement of the reaction. This condition has been discussed in previous studies. [22, 27]

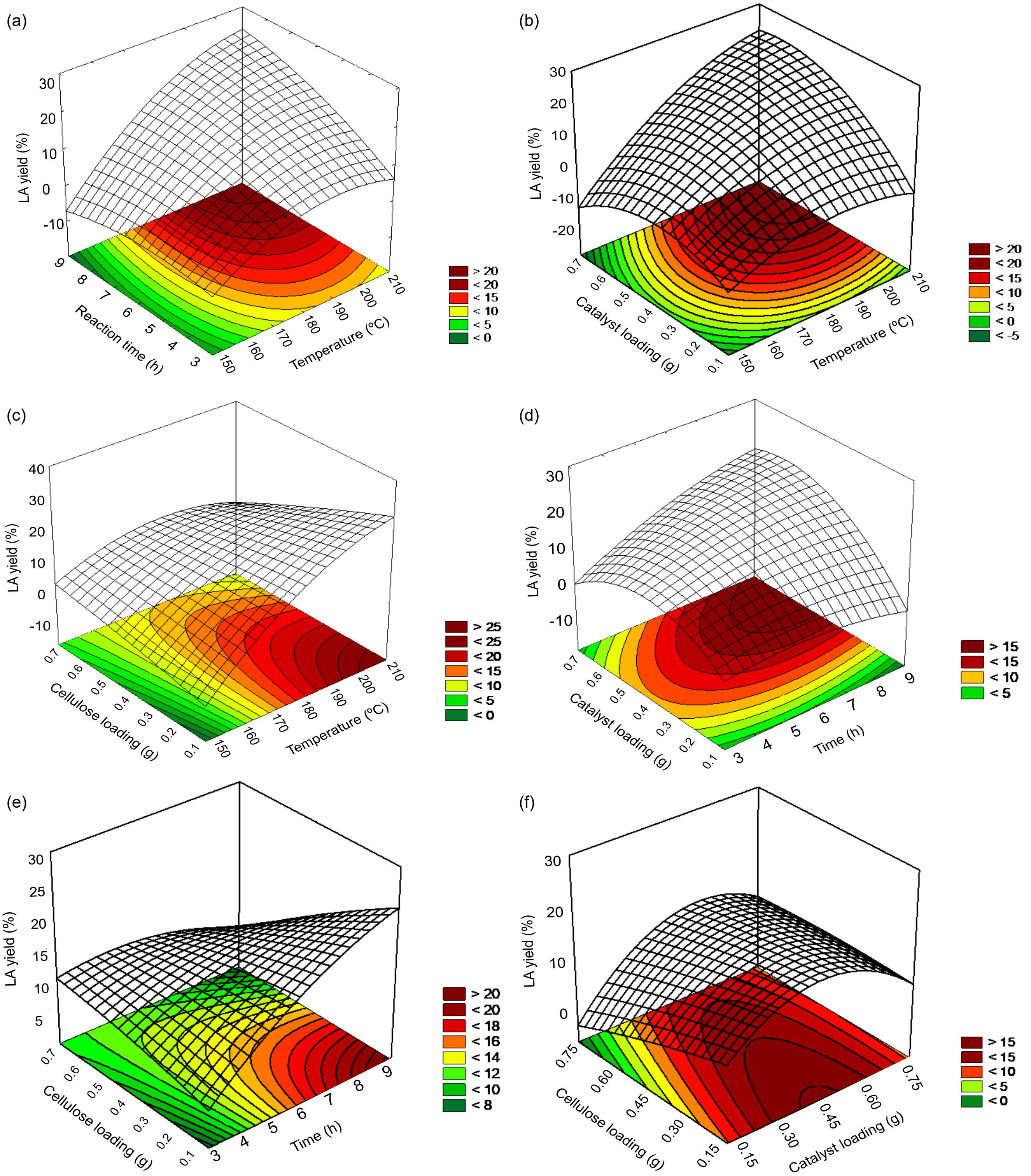

Fig. 2. 3D response surface plots of LA yield from cellulose versus different variables. **a)** temperature and time **b)** temperature and catalyst loading **c**) temperature and cellulose loading **d)** time and catalyst loading **e)** time and cellulose loading **f)** catalyst and cellulose loading.

Optimization study and application of biomass to LA

From the model equation, the optimum condition was predicted to obtain high yield of LA from cellulose. The optimum condition predicted LA yield is 26.7%, which can be achieved at reaction temperature of 200 °C, reaction time of 7 h, catalyst dosage of 0.6 g, and feedstock loading of 0.3 g. Further test was carried out to verify the model equation by evaluate LA yield experimentally at optimum condition given previously. The observed LA yield was 27.2%, indicating an error of 1.8% of the observed value toward the predicted values.

The potentials of OPF and EFB for LA production over HY-IL catalyst were investigated. LA yields of 24.1% and 21.3% were obtained from OPF and EFB, respectively, under optimum conditions. The LA yield from OPF was higher than from EFB due to the higher cellulose content in OPF. The efficiency of LA production from OPF and EFB was 75% and 72%, respectively. The result from the present study demonstrates that more than half of the cellulose content in the OPF and EFB was converted to LA using HY-IL catalyst. Overall, 100% efficiency of biomass conversion to LA is not possible due to parallel reaction and decomposition of biomass component to other compounds [23].

CONCLUSION

High LA yield could be obtained from cellulose using HY-IL catalyst under optimum process conditions. Four variables namely reaction temperature, reaction time, catalyst loading, and cellulose loading, influence the LA production from cellulose. The linear effect of reaction temperature has the most significant effect on LA yield from cellulose. The optimum condition for LA yield (27.2%) is as follows: 200 °C reaction temperature, 7 h reaction time, 0.6 g catalyst loading, and 0.3 g cellulose loading. The utilization of lignocellulosic biomass at optimum conditions produced 24.1% and 21.3% LA yield from OPF and EFB, respectively. Meanwhile, the process efficiency of LA production from OPF and EFB were 75% and 72%, respectively. High LA yield could be obtained from samples with large amount of cellulose. The results from this work can provide the preliminary information for the potential of oil palm waste to be converted to high-value products.

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REFERENCES

[1] Tong, X., Y. Ma, and Y. Li, Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes. *Applied Catalysis A: General*, 2010. 385(1): p. 1-13.
[2] Rizal, N., M. Ibrahim, M.R. Zakaria, E. Bahrin, S. Abd-Aziz, and M. Hassan, Combination of superheated steam with Laccase pretreatment together with size reduction to enhance enzymatic hydrolysis of oil palm biomass. *Molecules*, 2018. 23: p. 811.
[3] Loh, S.K., The potential of the Malaysian oil palm biomass as a renewable energy source. *Energy Conversion and Management*, 2017. 141: p. 285-298.
[4] Chang, S.H., An overview of empty fruit bunch from oil palm as feedstock for bio-oil production. *Biomass and Bioenergy*, 2014. 62: p. 174-181.
[5] Zahari, M.A.K.M., M.R. Zakaria, H. Ariffin, M.N. Mokhtar, J. Salihon, Y. Shirai, and M.A. Hassan, Renewable sugars from oil palm frond juice as an alternative novel fermentation feedstock for value-added products. *Bioresource Technology*, 2012. 110: p. 566-571.
[6] Goh, C.S., K.T. Tan, K.T. Lee, and S. Bhatia, Bio-ethanol from lignocellulose: Status, perspectives and challenges in Malaysia. *Bioresource Technology*, 2010. 101(13): p. 4834-4841.
[7] Morone, A., M. Apte, and R.A. Pandey, Levulinic acid production from renewable waste resources: Bottlenecks, potential remedies, advancements and applications. *Renewable and Sustainable Energy Reviews*, 2015. 51: p. 548-565.
[8] Qing, Q., Q. Guo, P. Wang, H. Qian, X. Gao, and Y. Zhang, Kinetics study of levulinic acid production from corncobs by tin tetrachloride as catalyst. *Bioresource Technology*, 2018. 260: p. 150-156.
[9] Li, X., X. Lu, S. Nie, M. Liang, Z. Yu, B. Duan, J. Yang, R. Xu, L. Lu, and C. Si, Efficient catalytic production of biomass-derived levulinic acid over phosphotungstic acid in deep eutectic solvent. *Industrial Crops and Products*, 2020. 145: p. 112154.
[10] Mikola, M., J. Ahola, and J. Tanskanen, Production of levulinic acid from glucose in sulfolane/water mixtures. *Chemical Engineering Research and Design*, 2019. 148: p. 291-297.
[11] Dutta, S., I.K.M. Yu, D.C.W. Tsang, Z. Su, C. Hu, K.C.W. Wu, A.C.K. Yip, Y.S. Ok, and C.S. Poon, Influence of green solvent on levulinic acid production from lignocellulosic paper waste. *Bioresource Technology*, 2020. 298: p. 122544
[12] Shen, J. and C.E. Wyman, Hydrochloric acid-catalyzed levulinic acid formation from cellulose: data and kinetic model to maximize yields. *AIChE Journal*, 2012. 58(1): p. 236-246.
[13] Khan, A.S., Z. Man, M.A. Bustam, C.F. Kait, A. Nasrullah, Z. Ullah, A. Sarwono, P. Ahamd, and N. Muhammad, Dicationic ionic liquids as sustainable approach for direct conversion of cellulose to levulinic acid. *Journal of Cleaner Production*, 2018. 170: p. 591-600.
[14] Hu, L., G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin, and S. Liu, Catalytic conversion of biomass-derived carbohydrates into fuels and chemicals via furanic aldehydes. *RSC Advances*, 2012. 2(30): p. 11184-11206.
[15] Zhang, Q., S. Zhang, and Y. Deng, Recent advances in ionic liquid catalysis. *Green Chemistry*, 2011. 13(10): p. 2619-2637.
[16] Tao, F., H. Song, and L. Chou, Catalytic conversion of cellulose to chemicals in ionic liquid. *Carbohydrate Research*, 2011. 346(1): p. 58-63.
[17] Ren, H., Y. Zhou, and L. Liu, Selective conversion of cellulose to levulinic acid via microwave-assisted synthesis in ionic liquids. *Bioresource Technology*, 2013. 129(0): p. 616-619.
[18] Xu, H., H. Zhao, H. Song, Z. Miao, J. Yang, J. Zhao, N. Liang, and L. Chou, Functionalized ionic liquids supported on silica as mild and effective heterogeneous catalysts for dehydration of biomass to furan derivatives. *Journal of Molecular Catalysis A: Chemical*, 2015. 410: p. 235-241.
[19] Wei, W. and S. Wu, Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst. *Fuel*, 2018. 225: p. 311-321.
[20] Li, X., R. Xu, Q. Liu, M. Liang, J. Yang, S. Lu, G. Li, L. Lu, and C. Si, Valorization of corn stover into furfural and levulinic acid over SAPO-18 zeolites: Effect of Brønsted to Lewis acid sites ratios. *Industrial Crops and Products*, 2019. 141: p. 111759.
[21] Alonso, D.M., J.M.R. Gallo, M.A. Mellmer, S.G. Wettstein, and J.A. Dumesic, Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. *Catalysis Science & Technology*, 2013. 3(4): p. 927-931.
[22] Ramli, N.A.S. and N.A.S. Amin, Optimization of renewable levulinic acid production from glucose conversion catalyzed by Fe/HY zeolite catalyst in aqueous medium. *Energy Conversion and Management*, 2015. 95: p. 10-19.
[23] Ya'aini, N., N.A.S. Amin, and M. Asmadi, Optimization of levulinic acid from lignocellulosic biomass using a new hybrid catalyst. *Bioresource Technology*, 2012. 116: p. 58-65.
[24] Gogoi, P., A. Dutta, P. Sarma, and R. Borah, Development of Brönsted–Lewis acidic solid catalytic system of 3-methyl-1-sulfonic acid imidazolium transition metal chlorides for the preparation of bis(indolyl)methanes. *Applied Catalysis A: General*, 2015. 492.
[25] Arya, K., D.S. Rawat, and H. Sasai, Zeolite supported Bronsted-acid ionic liquids: an eco approach for synthesis of spiro[indole-pyrido[3,2-e]thiazine] in water under ultrasonication. *Green Chemistry*, 2012. 14(7): p. 1956-1963.
[26] Sweygers, N., R. Dewil, and L. Appels, Production of levulinic acid and furfural by microwave-assisted hydrolysis from model compounds: effect of temperature, acid concentration and reaction time. *Waste and Biomass Valorization*, 2018. 9(3): p. 343-355.
[27] Ya'aini, N. and N.A. Saidina Amin, Catalytic conversion of lignocellulosic biomass to levulinic acid in ionic liquid. *BioResources*, 2013. 8.