

Kinetic study on oil palm biomass conversion to levulinic acid via indium trichloride-ionic liquids

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Abstract. This study investigates the kinetics of depolymerisation reaction of oil palm mesocarp fiber biomass conversion to levulinic acid via Bronsted-Lewis acidic ionic liquids catalyst. An eco-friendly catalyst was developed by coupling Lewis acid indium trichloride with a noncorrosive acidic mono-alkylated ionic liquids, 1-methylimidazolium hydrogen sulfate, for the production of levulinic acid in a greener perspective. The kinetic experiments were conducted at mild temperatures ranged from 135 to 175°C at varying time of 1.5 to 5h. A kinetic model based on the pseudo first-order reaction was established to describe the behaviour of catalytic LA production. The activation energy of the depolymerisation reaction was calculated to be 61.8 kJ mol⁻¹, which is comparatively lower than the previous reported values via various catalytic means of LA production from various biomass feedstock.

1. Introduction

Lignocellulosic biomass, such as agricultural waste, has become a particularly appropriate bioenergy feedstock due to its abundance, low cost and environmental benefits. As Malaysia has as a rich oil palm industry, a tremendous amount of oil palm biomass residues is generated each year. For instance, a palm fruit could generate up to 11% of mesocarp fiber (OPMF) biomass when the oil has been extracted [1]. This cellulosic biomass can be depolymerised into various chemicals, such as sugar, furfural, 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA) [2]. Among these, LA has been identified as a versatile intermediate chemical with dual functional groups, i.e. acidic carboxyl group (COOH) and ketone carbonyl group (C=O), which provide a wide range of functionality and reactivity for the conversion into various high end chemicals [3]. Specifically, LA can be upgraded into a variety of biofuel molecules such as 2-methylfuran, γ -valerolactone, valeric esters and levulinate esters [4]. Nonetheless, the economic ways of producing LA from biomass feedstock is yet to advance to a larger scale and hence is of high interest to researchers.

Conventionally, the conversion of LA from biomass can be enhanced by the addition of mineral acids or heterogenous acid catalysts. However, heterogenous acid catalysts are naturally unstable due to its rapid deactivation and mineral acids encounter corrosion issues [5]. These limitations drive the researchers to seek for alternative catalysts such as ionic liquids (ILs). ILs is a new generation of reaction media which is green and could serve in various applications, particularly in the processing of energy conversion materials by primarily disrupting the hydrogen bonds between the molecules [6].



Their negligible vapour pressure, non-flammable, reduce energy consumption in processing and recyclable, form the basis of being classified as “green” dual solvent-catalysts [7].

The present work focuses on the kinetic study of LA production from OPMF biomass conversion via ILs. A Bronsted-Lewis acidic ILs (BLAILs), which made of an eco-friendly Lewis acid indium trichloride (InCl_3) coupled with a noncorrosive acidic mono-alkylated ILs, 1-methylimidazolium hydrogen sulfate ($[\text{HMIM}][\text{HSO}_4]$), was used to catalyse the depolymerisation reaction of OPMF to LA. A kinetic model was established to depict the experimental data, alongside with the determination of the rate constant and activation energy of the reaction.

2. Materials and Methods

2.1. Materials

OPMF sample was collected at Seri Ulu Langat Palm Oil Mill, Dengkil, Selangor. The ILs, $[\text{HMIM}][\text{HSO}_4]$, was purchased from Sigma-Aldrich, USA, with a purity of $\geq 95\%$. A standard analytical grade of LA (99%) and indium (III) chloride tetrahydrate, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (97%) were also purchased from Sigma-Aldrich, USA. Analytical grade ethyl acetate (RCI Labscan) was supplied by EOS Scientific Limited (Selangor, Malaysia).

2.2. Characterisation of OPMF composition

The compositions of OPMF were determined by thermal gravimetric analysis (TGA) using a Mettler Toledo TGA/DSC1, followed by cellulose and hemicellulose determination analysis according to the method reported by Teramoto et al. [8]. For TGA analysis, the biomass samples were heated in a platinum cell with a scanning rate of $10^\circ\text{C}/\text{min}$, from 30 to 700°C , under a nitrogen flow rate of 20 ml min^{-1} [9].

2.3. Kinetic experimental study: Depolymerisation reaction

Depolymerisation reactions were carried out at different temperatures (135 to 175°C), at a fixed ILs-to-biomass ratio of 6.6:1 (w/w) and water content of 22.7% (w/w), at varying reaction time (1.5 to 5h), in a pressure vessel (Chemglass, USA). Upon completion, the reaction mixture was isolated and analysed.

2.4. Products isolation

The reaction mixture was extracted three times with 1:1 (v/v) ethyl acetate and transferred into a centrifuge tube. The solution was centrifuged at 2,000 rpm for 5 min. This resulted the formation of a two-layered solution, i.e., the upper layer of organic phase and the bottom layer of aqueous phase. The organic liquid layer was withdrawn from the upper layer and evaporated to dryness at 50°C for 30 min using a rotary evaporator (Heidolph, Germany). The content was reconstituted to 2 ml of ethyl acetate, and further diluted with ethyl acetate whenever necessary. The sample was then proceed for GC-MS analysis.

2.5. Products analysis

LA content was determined by using GC (Perkin Elmer Clarus 680) equipped with a MS detector and fused silica capillary column (HP-FFAP, 30 m x 0.32 mm x 0.25 μm). The autosampler injection volume was 1.0 μl in the split mode ratio of 50:1. The injection port was maintained at 240°C , while the operating temperature for oven was initially set at 90°C for 3 minutes, then gradually increased to 230°C at a rate of $10^\circ\text{C}/\text{min}$, and held at the final temperature for 10 minutes. A solvent delay of 2 minutes was applied. Helium was used as carrier gas at a constant flow of 1.0 ml min^{-1} . LA content was identified with GC-MS library system (NIST MS search library) and further confirmed with injection of standard solution. The quantitative analysis of LA was conducted with a 6-point calibration curve ($R^2 > 0.99$), by using an internal standard of butyric acid ($>99\%$, Sigma-Aldrich, USA). The standard deviations (σ) of triplicate data obtained for all yields were ranged from 0.9-4.2%

with average at $\pm 3\%$. The actual yield, theoretical yield and efficiency of LA were calculated by Equations (1)-(3):

$$\text{LA yield (\%)} = \frac{\text{Amount of LA}}{\text{Weight of initial biomass loading}} \times 100\% \quad (1)$$

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

$$\text{where } \frac{\text{Molecular weight of LA}}{\text{Molecular weight of cellulose}} = \frac{116}{162} = 0.71$$

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

where efficiency refers to the efficiency of biomass conversion to LA calculated based on cellulose content.

3. Results and discussions

3.1. Characterisation of OPMF compositions

The thermal degradation of TGA gave three distinct stages of weight losses for both samples. The weight losses are due to the evaporation of residual water, volatilization of holocellulose and degradation of lignin. The TGA analysis, followed by cellulose and hemicellulose characterisation studies revealed that OPMF contains 4.31% moisture, 16.29% lignin, 23.12% ash, 29.96% cellulose and 26.32% hemicellulose [9].

3.2. Kinetic study

The conversion of OPMF biomass to LA is a multi-step process which involves various intermediate products. The cellulose fraction (glucan) is depolymerised to glucose, which further dehydrated to 5-HMF and finally rehydrate into LA [10]. In this study, a simplified model was proposed based on sole LA efficiency, which exclude the role of intermediate products. A pseudo-first order irreversible reaction was established by assuming glucan was directly depolymerised into LA. The model is proposed as follows:



Figure 1(a) illustrates the results of LA efficiency at different reaction temperature and time. The 5-HMF concentrations measured were low for all conditions studied, presumably the compound had been converted to LA. Some trace amount of by-products were not computed, as the possible side reactions were considered negligible. The LA efficiency was increased by increasing temperature and prolonging reaction time. This results were in the agreement with Ramli and Amin [11].

As shown in Figure 1(b), the line graph between $-\ln(1-X)$ and time at five different temperatures support the hypothesis of pseudo-first order reaction. Table 1 summaries the rate constant (k) and the corresponding correlation coefficients (R^2) of linear fitting for the temperatures studied. The activation energy (E_a) and exponential factor (A) were obtained by applying the Arrhenius equation as follows.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

where k is the rate constant, represents the number of effective collisions among the reactants, A is the exponential factor, represents the total number of collisions, R is the universal gas constant and E_a is the required activation energy.

Figure 1(c) shows strong linearity ($R^2 = 0.99$) between $\ln k$ and $1/T$ for the range of temperature studied. The E_a determined from the slope of the line was 61.8 kJ mol^{-1} , while A calculated from the intercept was $5.9 \times 10^6 \text{ min}^{-1}$. As such, the Arrhenius equation for this ILs catalytic system for the production of LA from OPMF biomass conversion could be written as:

$$\ln k = 15.59 - 7.43 / T$$

where k is the rate constant (min^{-1}) and T is the temperature (K).

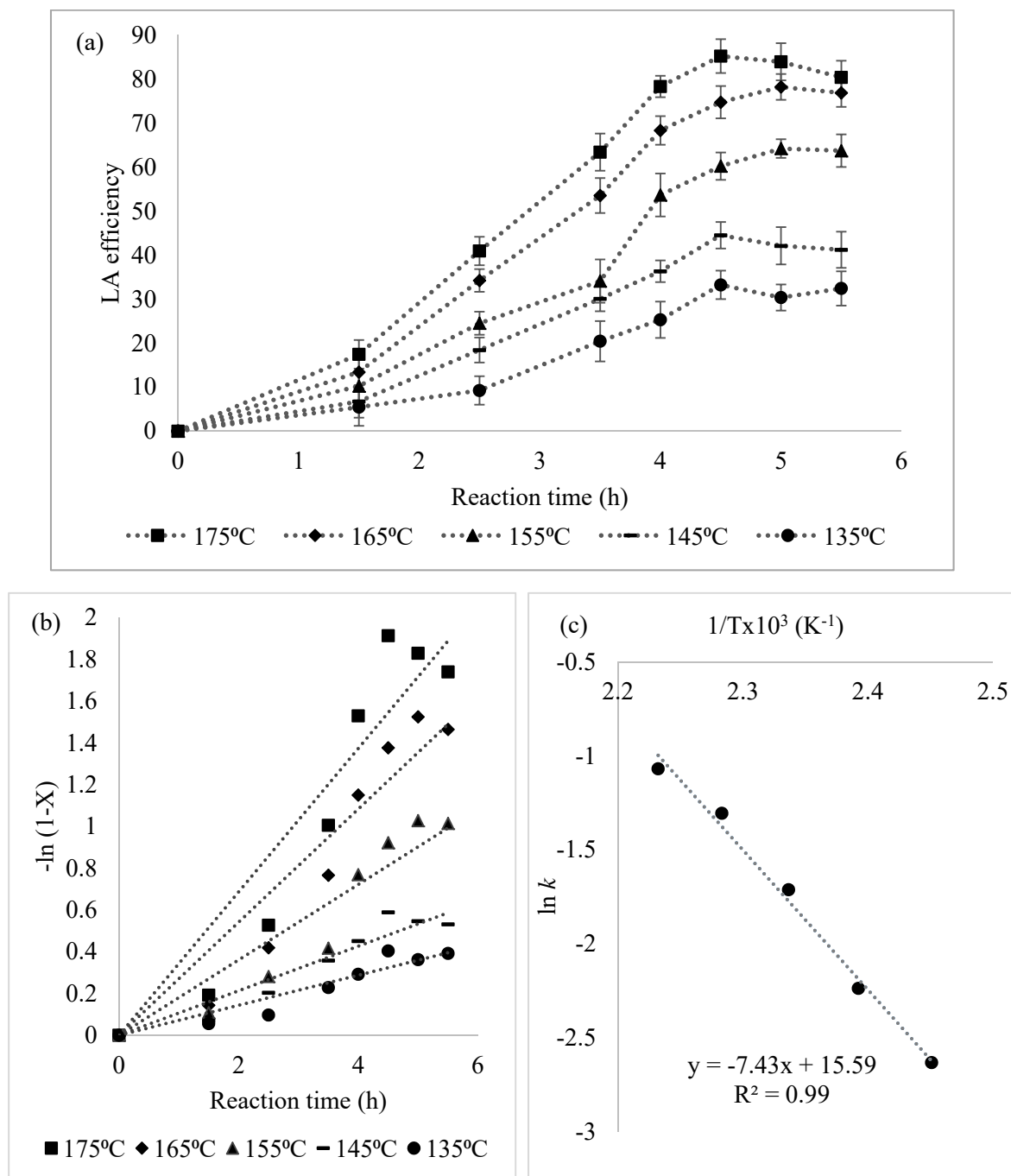


Figure 1. (a) LA efficiency from OPMF biomass conversion via ILs, (b) $-\ln(1-X)$ versus reaction time at different reaction temperatures, (c) Arrhenius plot of $\ln k$ versus $1/T \times 10^3$.

Table 1. Rate constant (k) and correlation coefficients (R^2) for the LA efficiency at different temperatures.

Temperature ($^{\circ}\text{C}$)	Rate constant, k (min^{-1})	Correlation coefficient, R^2
135	0.0720	0.9072
145	0.1068	0.9222
155	0.1806	0.8915
165	0.2711	0.9131
175	0.3436	0.8924

The E_a and A obtained in the present study were lower than those reported for catalytic conversions of various biomass to LA via metal salts (FeCl_3) [10,12] and mineral acids (H_2SO_4) [13-15]. This suggested InCl_3 -[HMIM][HSO_4] catalytic system has the immense potential to be used in a large scale sustainable LA production from renewable biomass feedstock.

4. Conclusions

OPMF biomass was converted to LA via InCl_3 -[HMIM][HSO_4] for a greener perspective. The kinetic study suggested that the InCl_3 -[HMIM][HSO_4] catalysed depolymerisation was a pseudo first-order reaction with a relatively lower E_a of 61.8 kJ mol^{-1} . A kinetic model was proposed to predict the LA efficiency for the conversions.

5. References

- [1] Nordin N I A A, Ariffin H, Andou Y, Hassan M A, Shirai Y, Nishida H, Yunus, W M Z W, Karuppuchamy S and Ibrahim N A 2013 *Molecules* **18** 9132
- [2] Chang C, Xu G and Jiang X 2012 *Bioresource Technology* **121** 93
- [3] Morone A, Apte M and Pandey R A 2015 *Renewable and Sustainable Energy Reviews* **51** 548
- [4] Koivisto E, Ladommatos N and Gold M 2015 *Energy & Fuels* **29** 5875
- [5] Mukherjee A, Dumont M J and Raghavan V 2015 *Biomass and Bioenergy* **72** 143
- [6] Eshetu G G, Armand M, Ohno H, Scrosati B and Passerini S 2016 *Energy & Environmental Science* **9** 49
- [7] Badgujar K C and Bhanage B M 2015 *Bioresource Technology* **178** 2
- [8] Teramoto Y, Lee S H and Endo T 2009 *Bioresource Technology* **100** 4783
- [9] Tiong Y W, Yap C L, Gan S, and Yap W S P 2017 *Chemical Engineering Transactions* **56** 1021
- [10] Dussan K, Girisuta B, Haverty D, Leahy J J and Hayes M H B 2013 *Bioresource Technology* **149** 216
- [11] Zheng X, Zhi X, Gu X, Li X, Zhang R and Lu X 2017 *Fuel* **187** 261
- [12] Ramli N A S and Amin N A S 2016 *Chemical Engineering Journal* **283** 150
- [13] Zhi Z, Li N, Qiao Y, Zheng X, Wang H and Lu X 2015 *Industrial Crop and Products* **76** 672
- [14] Chang C, Ma X and Cen P 2009 *Chinese Journal of Chemical Engineering* **17** 835
- [15] Girisuta B, Dussan K, Haverty D, Leahy J J and Hayes M H B 2013 *Chemical Engineering Journal* **217** 61

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