Journal of Clean Energy Technologies, Vol. 4, No. 1, January 2016

The Effect of Temperature on Sulfuric Acid-Catalyzed Hydrolysis of Oil Palm Frond to Levulinic Acid

A. Awaluddin, A. Kurnia, A. Prayitno, E. Saputra, and Saryono

Abstract—**The levulinic acid (LA), one of platform chemicals, could be potentially generated from an oil palm frond, thus possibly replacing a fossil source as a precursor to produce a wide range of chemicals. This research focuses on the conversion of the oil palm frond into levulinic acid using sulfuric acid as homogeneous acid catalyst. The experiments were conducted in the ampoule reactor (150 mm of length, 4 mm of inside diameter, 7 mm of outside diameter) with the conditions of 1 w/v % of the ratio of biomass weight to acid volume, 150-190 °C of reaction temperature, 1 M of sulfuric acid concentration and 0-240 minutes of reaction times. The maximum yield of levulinic acid formed is 31.28% based on the cellulose content in the oil palm frond. The conversion of the oil palm frond into LA seems to follow *pseudo*-first order reaction and kinetic model developed by previous researcher.**

***Index Terms*—Levulinic acid, oil palm frond, *pseudo*-first order reaction.**

I. INTRODUCTION

Levulinic acid (LA) is an organic compound with the formula $CH_3C(O)CH_2CH_2CO_2H$. This acid is considered as a *platform chemical*, since it could be used as a precursor to produce a wide variety of chemicals [1]. The derivate of LA have many applications such as resin polymer, dye textile and fuel additive [2]. This versatile acid could be produced from renewable sources such as a biomass through acid-catalyzed hydrolysis reaction [1].

Indonesia is the largest palm oil plantation in the world. The plantation produces not only crude palm oil (CPO) as the major product of palm oil industry, but also generates by-products such as solid empty fruit bunches and liquid wastes. Other material produced is oil palm frond as agricultural residues. Agricultural residues are one of the most potential biomass sources for production of bio-chemicals such as LA, since they could not be used as food sources and are available in large quantity [3]. To date, oil palm frond has not been effectively utilized in the most part of Indonesia and could be a potential candidate as raw materials for levulinic acid production. As largest palm oil plantation in Indonesia, Riau Province with 1,926,859 hectare of palm oil plantation in 2012, produced 60.262.515 ton of oil palm frond as wastes [4]. Thus, there are many oil palm fronds available in that Province that could use as feedstock for production of LA.

The conversion of biomass into levulinic acid have been studied previously using acid-catalyzed hydrolysis reaction in which either hydrochloric or sulfuric acid was used as the acid catalyst [5]. The sulfuric acid is prefer than the hydrochloric counterpart as it is cheaper , more effective [3] and produce a higher proportion of levulinic acid [6].

This research focuses on the production of levulinic acid from oil palm frond using sulfuric acid as acid catalyst. The reaction temperatures are varied in the effort to optimize the levulinic acid production. The conversion of oil palm frond into levulinic acid is studied using kinetic model previously developed by Shen [1].

II. EXPERIMENTAL

The oil palm fronds used in this experiment were obtained from palm plantation in Pantai Cermin Area, Kampar District, Riau Province. The fronds were first air-dried under sun radiation, followed by milled using distilled water to get slurry. The slurry was then dried to produce powder, followed by 100 mesh-filtration. The resulting powders, dissolved in solution of M sulfuric acid, were placed into ampoule and other end of ampoule was then sealed with a torch to avoid evaporation of the sample when heated. The solutions were heated to 150, 170, 180 and 190 °C with the reaction time based on the glucose content in the sample [7]. The ratio between powder and volume of the sulfuric acid is 1 w/v% (1 gr /100 mL). The reaction was quenched in an ice-water bath (4 °C) to stop the reaction. The ampoule was opened and the liquid was diluted with reverse osmosis water and separated from the solids using centrifuge for 15 minutes. The composition of the solution was determined using high-performance liquid chromatography (HPLC).

III. RESULTS AND DISCUSSION

A. Reaction Products

The conversion of oil palm frond into LA is believed to follow reaction pathway schematically given in Scheme 1. The broken of the polymer chains of cellulose of the oil palm frond into small fragments is considered as the first of the reaction, followed by the formation of glucose. The glucose is then decomposed into 5-hydroxymethylfurfural (HMF), which is further converted to levulinic acid and formic acid. A typical example of an HPLC chromatogram of the

---

Manuscript received October 10, 2014; revised January 20, 2015.

A. Awaluddin and Saryono are with Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Riau, Pekanbaru, Indonesia (e-mail: amirawaluddin01@gmail.com, saryono_ur@yahoo.com).

A. Kurnia was with Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Riau, Pekanbaru, Indonesia (e-mail: ipon.sandi@ymail.com).

A. Prayitno is with Department of Mechanical Engineering, Faculty of Engineering, University of Riau, Pekanbaru, Indonesia (e-mail: gendon_tho@yahoo.co.uk).

E. Saputra is with Department of Chemical Engineering, Faculty of Engineering, University of Riau, Pekanbaru, Indonesia (e-mail: edysaputra_eng@yahoo.com).

DOI: 10.7763/JOCET.2016.V4.253

decomposition of the oil palm frond is given in Fig. 1. The peak at 10.14 minutes of retention time is due to the formation of glucose, whereas at 18.82 minutes is the typical peak for levulinic acid. Other smaller peaks are at 15.00 minutes (formic acid) and at 10.79 minutes (unknown).

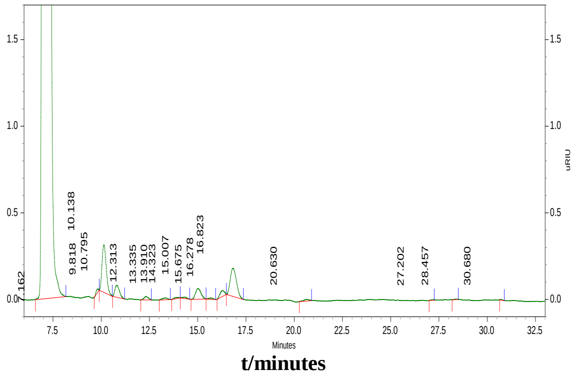


Fig. 1. Typical HPLC chromatogram for the acid-catalyzed hydrolysis of oil palm frond.

B. *The Effect of Temperature on LA Production*

The sulfuric acid-catalyzed conversion of the oil palm frond into LA was conducted with ratio of frond weight relative to acid volume of 0.01, catalyst concentration of 1M, reaction temperature of 150, 170, 180 and 190 ˚C. The composition of the reaction mixture was followed in time and a typical concentration profile is given in Fig. 2 to Fig. 5. The conversion of oil palm fronds into LA is believed to take place in the series of reactions indicated in the scheme 1 [1]. The oil palm fronds are first decomposed into smaller fractions, mainly glucose, then undergone dehydration to produce 5-hydroxymethylfurfural (HMF), which reacts with water in acidic condition to generate LA and formic acid. The formic acid probably formed was not shown in the Fig. 2 to Fig. 5 since it was not analysed using HPLC. During all experiments, dark-brown insoluble solid substances known as humans were formed. These are well-known products of side-reactions of the acid-catalyzed decompositions of glucose and HMF [7].

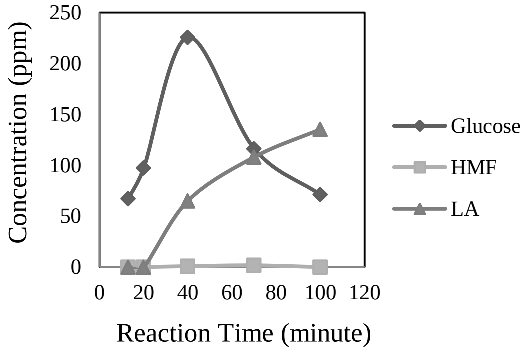


Fig. 2. Typical concentration profile during acid-catalyzed hydrolysis of oil palm frond (oil palm front intake = 1 wt %, H_2SO_4 =1 M, *T* =150 ℃).

The solids are believed to consist of mixture mainly of humin (typical composition: C, 63.1; H, 4.2) and some unreacted cellulose (C, 42.2; H, 6.1) [7]. As anticipated on the basis of Scheme 1, the concentrations of glucose displayed an optimum, which is 225 part per million (ppm). The maximum HMF concentrations obtained in all experiments were generally much lower than the maximum glucose concentration, which indicates that the conversion of HMF to levulinic acid (LA) and formic acid (FA) is much faster than the conversion of glucose to HMF. Fig. 2 to Fig. 5 also indicated that higher temperatures accelerate the rate of conversion of oil palm frond into glucose or LA. For example, at 150 ^{o}C (Fig. 2) it takes 40 minutes for glucose and 100 minutes for LA to attain maximum conversion. When temperature was raised to 170 ^{o}C, the maximum conversions for both glucose and LA were attainable within 20 minutes and 70 minutes, respectively. Higher temperatures led to shorter reaction time to achieve maximum conversion. The similar results were also observed by Girisuta [6] in which the temperature increase accelerates the reaction rates for the conversion of glucose into levulinic acid. This is due to the fact that at high temperature there is much more energy provided to a system such that the more collusion occurs among reactants and catalyst. This, of course, accelerates the rate of a reaction. Data from Fig. 2 to Fig. 5 showed that higher temperature led to lower concentration of LA.

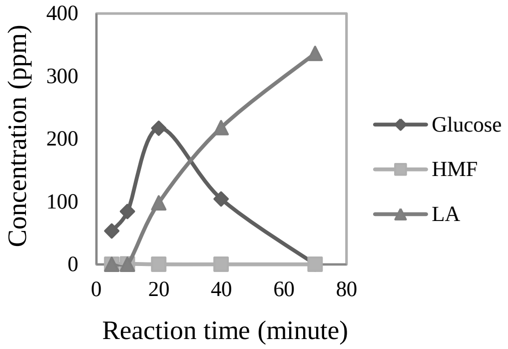


Fig. 3. Typical concentration profile during acid-catalyzed hydrolysis of oil palm frond (oil palm front intake = 1 wt %, H_2SO_4 =1 M, *T* =170 ℃).

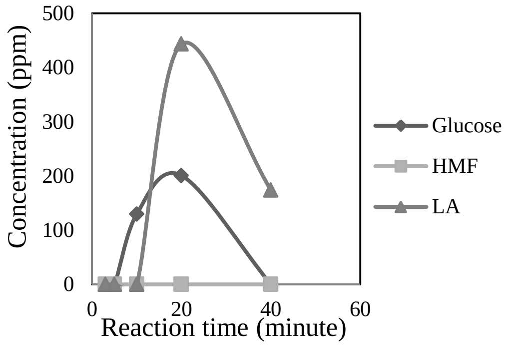


Fig. 4. Typical concentration profile during acid-catalyzed hydrolysis of oil palm frond (oil palm front intake = 1 wt %, H_2SO_4 =1 M, *T* =180 ℃).

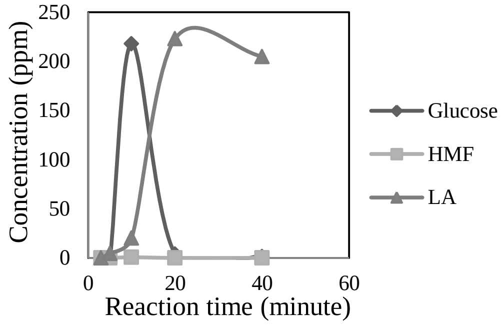


Fig. 5. Typical concentration profile during acid-catalyzed hydrolysis of oil palm frond (oil palm front intake= 1 wt %, H_2SO_4 =1 M, *T* =190 ℃).

Table I shows the yield of levulinic acid at different reaction temperatures. Although there is an increase of the LA yields from 150 to 170 ^oC, the yield at 190 ^oC is lower. Shen [1] reported similar results that the temperature rise led to lower yield of LA. It could be concluded that higher temperature only accelerates the rates of reaction of LA formation, whereas the yields of LA tend to lower. The lower yield at high temperature could be due to the decomposition of LA into decomposed solid products as proposed in scheme 1. This is supported by the fact that more solid products produced at high temperature.

TABLE I: THE YIELDS OF LA AT DIFFERENT TEMPERATURES

Reaction Tempera ture (^oC)	Reaction time (minute)	LA Concentration (mg/L)	*Yield* of LA Based on cellulose content
150	100	135,3	4,51
170	70	336,4	11,21
180	20	443,4	14,78
190	20	223,1	7,43

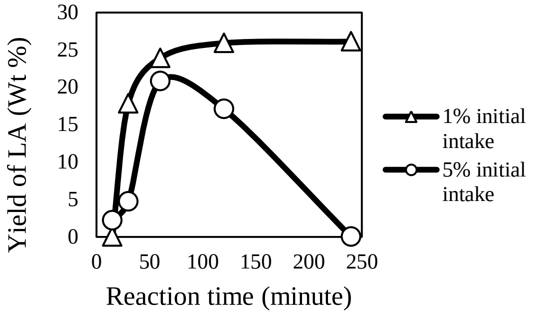
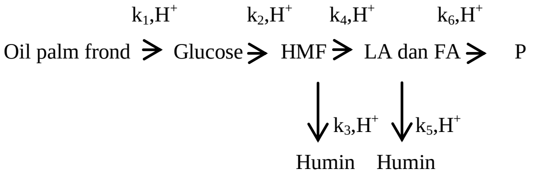


Fig. 6. Effect of initial intake of oil palm frond on yields of levulinic acid.

The yield of levulinic acid is also a function of the amount of initial intake, with high proportion of initial intake reduced the yields. This is illustrated in Fig. 6, where the yields of levulinic acid are plotted as a function of initial intake at two different initial intakes.

C. *Kinetic Conversion of Oil Palm Front into LA*

Like other biomasses under acidic condition at elevated temperatures, oil palm frond decomposes into a variety of products, through the intermediates such as glucose and 5-HMF, then decompose further into LA and formic acid. LA finally decomposes into final decomposed material P. The kinetic model applied for the conversion oil palm frond into LA is adopted from that developed by Shen [1] as shown in scheme 1. The kinetic data shown in Table II was obtained using the *Maple* Programme of 13 version and combined with *Polymath*.



Scheme 1. Model for LA formation from oil palm frond adopted from Shen [1].

Data from Table II show conflicting results with those from Fig. 2 to Fig. 5. The rate constant for the conversion of HMF to LA (k_4) is much lower than that for the conversion of glucose to HMF (k_2). This indicates that the conversion of glucose to HMF is much faster that that HMF to LA. As a result, the concentration of HMF would be much higher than that shown in Fig. 2 to 5. The activation energy shown in Table II also supports the data of rate constants. The activation energy of the conversion of glucose to HMF is also lower than that of the conversion of HMF to LA. This suggests that it requires higher energy to convert HMF to LA than glucose to HMF. Thus, HMF should have much higher concentration than that shown in Fig. 2 to Fig. 5. Similar results are also obtained by Shen [7] in which there are disagreements between results from experimental and kinetics model proposed.

TABLE II: THE RATE CONSTANTS AND ACTIVATION ENERGIES FOR EACH STEP OF REACTION

	k1	k_{glu}	k2	k3	k_{HMF}	k4	k5	k6
150 ^oC	0,001	0,104	0,104	0	0,017	0,012	0,005	N/A
170 ^oC	0,025	0,424	0,424	0	0,031	0,023	0,008	N/A
190 ^oC	0,495	0,33	0,33	0	0,262	0,255	0,007	N/A
Ea (J/mol)	36631	6839	7191	N/A	15771	17609	2120	N/A

where:

k_1 : Rate constant for the hydrolysis of oil palm frond to glucose;

k_{glu} : Rate constant for the decomposition of glucose;

k_2 : Rate constant for the conversion of glucose to HMF;

k_3 : Rate constant for the degradasion of glucose to humin;

k_{HMF} : Rate constant for the decomposition of HMF;

k_4 : Rate constant for the conversion of HMF to LA;

k_5 : Rate constant for the degradasion of HMF to humin;

k_6 : Rate constant for the degradasion of LA.

IV. CONCLUSION

The conversion of oil palm frond into LA has been successfully conducted using sulfuric acid-catalyzed reaction. The increase of temperatures accelerates the reaction rates of LA conversion, but the yields of LA decreases. The kinetic model adopted from the previous model has been applied to study the LA production. Both rate constants and activation energies obtained from this model do not support the experimental results; thus modified model is required to support experimental findings.

ACKNOWLEDGMENT

The authors would like to thank Prof. Erik Heeres from University of Groningen and Jenny from University of Parahiyangan for introducing this research area. The authors also thank the University of Riau for proving this financial research project.

REFERENCES

[1] J. Shen and C. E. Wyman, “Hydrochloric acid-catalyzed levulinic acid formation from cellulose: Data and kinetic model to maximize yields, ”

American Institute of Chemical Engineers Journal, vol. 58, no. 1, pp. 236-246, 2011.

[2] J. J. Bozell, L. Moens, Y. Wang, G. G. Neuenswander, S. W. Fitzpatrick, R. J. Bilski, and J. L. Jarnefeld, "Production of levulinic acid and use as a platform chemical for derived products," *Resources, Conservation and Recycling*, vol. 28, pp. 227-239, 2000.

[3] Q. Fang and M. A. Hanna, "Experimental studies for levulinic acid production from whole kernel grain sorghum," *Bioresource Technology*, vol. 81, pp. 187-192, 2002.

[4] K. S. Junjungan and A. Tarigan, "The use of oil palm frond as forage," in *Proc. Indonesian National Seminar on Cattle Technology and Veterinary*, 2007, pp. 417-424.

[5] B. Girisuta, L. P. B. M. Janssen, B. Danon, R. Manurung, and H. J. Heeres, "Experimental and kinetic modeling studies on the acid-catalyzed hydrolysis of the water hyacinth plant to levulinic acid," *Bioresource Technology*, vol. 99, pp. 8367-8375, 2008.

[6] B. Girisuta, L. P. B. M. Janssen, and H. J. Heeres, "A kinetic study on the conversion of glucose to levulinic acid," *Chemical Engineering Research and Design*, vol. 84, no. A5, pp. 339-349, 2006.

[7] B. Girisuta, L. P. B. M. Janssen, and H. J. Heeres, "A kinetic study on the acid catalyzed hydrolysis of cellulose to Levulinic acid," *Ind. Eng. Chem. Res*., vol. 46, pp. 1696-1708, 2007.

Amir Awaluddin was born in Kijang, on December 17, 1962. He completed the undergraduate study in the Department of Chemistry, Universitas Gadjah Mada (Indonesia) in 1988 and continued his master degree study in Department of Chemistry, University of Connecticut (USA) in 1993. Then he earned the PhD degree in School of Sciences, University of Salford (UK) in 2003.

He has been a lecturer in Department of Chemistry, Universitas Riau since 1989. His research interest includes the synthesis of manganese oxide microporous materials using various methods and conversion of biomass into biofuels and biochemicals. One of his recent publications is biomass conversion into bio-chemicals, such as "The conversion of the starch of dahlia tuber (*Dahlia variabilis*) into Levulinic acid," on Journal of Indonesian Chimia Acta, vol. 4, no. 1).

Prof. Dr. Amir Awaluddin has become a leader of Himpunan Kimia Indonesia-Cabang Riau (Indonesian Society of Chemistry-Riau Branch).

Arif Kurnia was born in Pekanbaru, on August 10, 1992. He started education in 1998 in Islamic Primary School As-Shoffa Pekanbaru. He continued his education at MTs Pekanbaru in 2004. In 2007-2010 he studied at SMA 5 Pekanbaru. After graduating from high school, he continued his education in the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Riau.

During the course, he was active in various activities, such as becoming a tutor of physics in Ganesha Operationand LSC. In 2012, he did practical work in the water laboratory at PT. RAPP. In addition, he also received a scholarship of PPA in 2012-2013 periods. He became a laboratory assistant of Inorganic Chemistry and Basic Chemical.

Arif Kurnia has conducted researches at the Laboratory of Inorganic Chemistry, Universitas Riau and Laboratory of Instruments Department of Chemical Engineering Faculty of Industrial Technology, Parahyangan University. In 2014 he successfully completed the study from the Department of Chemistry, University of Riau and the right holds a bachelor of science degree.

Adhy Prayitno was born in Tinjowan, on December 30, 1956. He completed the undergraduate study in the Department of Physics, Universitas Riau in 1985 and continued his master degree study in Department of Physic and Astronomy, Ball State University (USA) in 1995. Then he received his PhD degree in the field of control engineering, form University of Manchester (UK).

He has been a lecturer of Department of Chemical Engineering, Universitas Riau in 1988 until present. He has become a vice rector for planning and collaboration in Universitas Riau. He has published some articles in both national and international publications in the field of chemical engineering such as "Morphology and mechanical properties of palm based fly ash reinforced dynamically vulcanized natural rubber/polypropylene blends," *Procedia Chemistry*, vol. 4, pp. 146-153, 2012, and so on.

Dr. Adhy Prayitno was a member of The Institution of Engineers Indonesia.

Edy Saputra was born in Palembang, on January 29, 1973. He finished the under-graduate study in the Department of Chemical Engineering, Universitas Sriwijaya at 1996 and continued his master degree in Department of Chemical Engineering, Universitas Gadjah Mada. In 2013, he completed the PhD degree in Department of Chemical Engineering, Curtin University of Technology (Australia).

He has been a lecturer of Department of Chemical Engineering, Universitas Riau in 2000 until present. He has published some articles in both national and international publications in the field of chemical engineering such as "Shape-controlled activation of peroxymono-sulfate by single crystal α-Mn2O3 for catalytic phenol degradation in aqueous solution" *Applied Catalysis B: Environmental*, pp. 154-155, 2014, and so on.

Edy Saputra was a member of Indonesian Association of Catalysis and The Institution of Engineers Indonesia.

Saryono was born in Pariaman, on June 11, 1962. He completed the undergraduate study in the Department of Chemistry, Universitas Riau in 1988 and continued his master degree study in Department of Biochemistry, Institut Teknologi Bandung in 1991 and received PhD degree in Department of Biochemistry, Universitas Padjadjaran.

He has been a lecturer of Department of Chemistry, Universitas Riau in 1989 until present. He belongs to a reviewer team of Directorate of Higher Education, Republic of Indonesia. His research is focused on chemistry, biochemistry, and biotechnology process. He has published some articles in both national and international publications about biochemistry of *Dahlia variabilis* such as "Maximizing the function of dahlia tuber," *Indian Dahlia Ann*., 2000, p. 33-36, and so on.

Dr. Saryono has become a member of Himpunan Kimia Indonesia (Indonesian Society of Chemistry) and Perhimpunan Biokimia dan Biologi Molekuler Indonesia (Association of Indonesian Biochemistry and Molecular Biology).

Wind Energy