

Catalytic Conversion of Empty Fruit Bunch (EFB) Fibres into Lactic Acid by Lead (II) ions

Siew Xian Chin,^{a,b,*} Siti Masrinda Tasirin,^a Chi Hoong Chan,^b Chin Hua Chia,^{b,*} Soon Wei Chook,^b Sarani Zakaria,^b and Mohd Shaiful Sajab^b

Lactic acid (LA) is a potential platform chemical that can be produced from lignocellulosic biomass. The development of a cost-competitive, catalytic-based LA production system is gaining significant attention in modern biorefineries. A series of experimental study was carried out to investigate the chemocatalytic effect of the conversion of oil palm empty fruit bunch (EFB) fibers into lactic acid under hydrothermal conditions. Synthesis of chemicals from lignocellulosic biomass involves complex mechanisms because of the complex composition of the biomass. Therefore, experimental parameters, *i.e.*, temperature, Pb(II) concentration, and reaction time were studied. It was found that production of LA is highly dependent on the experimental conditions. In this study, the highest LA yield obtained from EFB fibers was > 46% (230 °C, 2 mM Pb(II) after 4 h of reaction). However, a similar yield can be achieved either using higher Pb(II) and shorter reactions time or *vice versa*. The selective production of chemical compounds (glucose, 5-hydroxymethyl furfural (5-HMF), furfural, levulinic acid, and lactic acid) from EFB fibers is highly dependent on the availability of Pb(II) ions.

Keywords: Green chemicals; Lactic acid; Acetic acid; Catalytic hydrothermal; Optimization

Contact information: a: Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia; b: Bioresources and Biorefinery Laboratory, School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia; *Corresponding authors: sxchin88@hotmail.com; chia@ukm.edu.my

INTRODUCTION

Since the 18th century, fossil fuels have powered the economy and brought an abundance of wealth to the world. Conventional energy sources, such as oil, natural gas, and coal, are the main choices for chemical and energy production. Although fossil fuel reserves are vast, they are finite resources that will be depleted with continuous exploitation (Folkedahl *et al.* 2011). Hence, interest in renewable resources, such as lignocellulosic biomass, has been re-discovered in the last decade, both in the production of fine chemicals or biofuels (Dusselier *et al.* 2013; Deuss *et al.* 2014).

Lignocellulosic biomass is abundant in nature, biodegradable, renewable, and cheap. Lignocellulosic biomass, such as forest biomass and agricultural crop residues, is considered an inedible plant material that does not compete with the food chain, such as potatoes, oat, wheat, barley, soybean, and rice. The shift from food crops to non-food biomass has a high potential for producing second-generation bio-based chemical feedstock while providing opportunities to capture high-value added products (Huber *et al.* 2006; Orozco *et al.* 2013). A huge amount of lignocellulosic biomass ($\sim 200 \times 10^9$ tons) is generated every year from agricultural activities, and most is still under-utilized (Lin and Tanaka 2006). Malaysia, as a major global palm oil producer, generates a large amount of

palm oil residues. To sustain economic growth, as palm oil production reaches maturity in Malaysia, it is imperative to find the next catalyst for growth in converting oil palm biomass into higher value products, such as fine chemicals (Ludin *et al.* 2014).

Lignocellulosic biomass is high in carbohydrate content (cellulose, hemicellulose), which can be readily hydrolyzed with dilute acid or enzymes then converted (in the presence of catalyst) into fine chemicals (Yan *et al.* 2015). This has attracted the attention of many researchers and industrial sectors. In Malaysia, oil palm EFB is one of the agricultural wastes with high contents of hemicelluloses and cellulose, approximately 39% and 27%, respectively (Chin *et al.* 2014). However, the current usage of EFB fibers primarily focuses on EFB as mulching material, organic fertilizer, or filler to reinforce composites. Oil palm EFB fibers can be one of the potential candidates for renewable resources, *i.e.*, to replace petro-based fine chemicals. This will not only resolve the waste management problem from the oil palm industry but also increase the country's revenue (National Biomass Strategy 2013).

Lactic acid (LA), a carboxylic acid, plays an important role in various biochemical processes. The US DOE has identified it as one of the top 15 platform chemicals from biorefinery carbohydrates (Werpy and Petersen 2004). LA acts as an important building-block chemical because it is an asymmetric carbon atom with the presence of two functional groups, which incorporates a lot of reactivity (Dusselier *et al.* 2013). Hence, it is widely used in the food, pharmaceutical, cosmetic, and chemical industries. LA in particular has received much attention recently as a monomer for the production of biodegradable polylactic acid (PLA) or polylactide (Hayashi and Sasaki 2005; de Clippel *et al.* 2012). Currently, lactic acid is produced by the fermentation method. Some of the major drawbacks of this method are up-scaling and environmental issues because of the generation of waste and purification process. Therefore, the chemocatalytic method may be one of the alternatives for obtaining lactic acid from biomass or sugar feedstock (Dusselier *et al.* 2013). Studies have reported the use of transition metal ions such as Zn(II), Ni(II), Cr(III), Al(III), and Pb(II) for biomass conversion to LA and levulinic acid (Peng *et al.* 2010; Wang *et al.* 2013; Sitompul *et al.* 2014). Wang *et al.* (2013) reported that Pb(II) ions are one of the most effective metal ions for the conversion of lignocellulosic materials into LA. Therefore, Pb(II) ions were chosen as the catalyst in this study.

In the present study, oil palm EFB fibers, a major agricultural biomass in Malaysia, were used to produce LA using a thermo-catalytic approach assisted by Pb(II) ions. This study aims to provide useful information and basic data for the practical use of Pb(II) in the conversion of EFB fibers into lactic acid. The mechanism and reaction pathway of the decomposition of EFB fibers are postulated for optimization purposes. This will not only open numerous possibilities for future research on chemical conversion of EFB fibers, but also fill voids in existing research. Additionally, despite the inevitable yield of humic products during catalytic conversion of EFB, the study and the separation of these products are not the main interest of the current study.

EXPERIMENTAL

Materials and Chemicals

Oil palm EFB fibers were purchased from Szetech Engineering Sdn. Bhd, located in Selangor, Malaysia. The fibers were sieved into sizes ranging from 150 to 500 μm , followed by drying at 105 $^{\circ}\text{C}$ before ball milling (BM) for 24 h. A SHQM planetary ball

mill (Chun Long instrument, Lianyungang City, Jiangsu Province, China) with four ceramic milling cylinders (50 mL) was used for the ball milling process. The EFB fibers were placed into each cylinder containing 10 ($\varnothing=10$ mm) and 40 ($\varnothing=6$ mm) ceramic balls. The mill was rotated horizontally at a constant speed of 230 rpm for 24 h. After that, the EFB fiber samples were stored in a desiccator for further use. The moisture content of the EFB fibers was measured using a moisture analyzer (MX-50, AND Company, Japan). After ball milling, the size of the EFB fibers was between 40 and 63 μm .

The analytical grade chemicals sodium hydroxide (NaOH, purity $\geq 99\%$), sulfuric acid (H_2SO_4 , purity 95% to 98%), lead (II) nitrate (purity $\geq 99\%$), and levulinic acid (purity $\geq 99.5\%$) were purchased from Merck (Darmstadt, Germany). Glucose (purity $\geq 99.5\%$), xylose (purity $\geq 99.5\%$), lactic acid (purity $\geq 99.5\%$), 5-HMF (purity $\geq 99.5\%$), furfural (purity $\geq 99.5\%$), and formic acid ($\geq 95\%$) were purchased from Sigma Aldrich (Shanghai, China).

Methods

Conversion of EFB fibers into LA and other fine chemicals

The reaction was carried out using a 60-mL high-pressure stainless steel Teflon®-lined autoclave. The autoclave was heated in a furnace at high temperature (170 to 230 $^{\circ}\text{C}$) for a fixed time. For a typical run, 0.1 g of EFB fibers was mixed with 20 mL of Pb(II) ion solution and heated at various temperatures and times. Upon completion, the autoclave was quenched in an ice bath to stop the reaction. The hydrolysate was collected by filtration. The chemical composition of the hydrolysate, including glucose, fructose, furfural, 5-HMF, LA, levulinic acid, acetic acid, LA, and other by-products, was measured using a high-performance liquid chromatography (HPLC) system (The Agilent 1260 Infinity Quaternary, USA), a Hi-Plex H column with a refractive index (RI) detector operating at 55 $^{\circ}\text{C}$, and a UV detector at 280 nm. H_2SO_4 (5 mmol) was used as the mobile phase at a flow rate of 0.6 mL/min.

Each compound was calibrated by its standard solutions with ten different concentrations (low to high concentration) (*e.g.*, 0.01 to 0.05 g/L and 0.1 to 0.5 g/L). All standard calibration curves obtained with $R^2 > 0.998$ were used for quantitative calculation. We evaluated the actual yield of LA from both C_6 and C_5 monomeric sugar units of the EFB fibers. The LA yield was calculated as follows:

$$\text{Yield of LA} = \frac{\text{mole of LA produced}}{[2(\text{mole of C}_6 \text{ units}) + (\text{mole of C}_5 \text{ unit})]} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Conversion of Raw and Ball-Milled EFB Fibers into Lactic Acid

The raw material (EFB fibers) used in this study was the same as that used in previous work by the authors (Chin *et al.* 2015). The EFB fibers were analyzed for glucan, xylan, lignin, water extractives, ethanol extractives, and ash content using NREL's laboratory method (Sluiter *et al.* 2008, 2010). The contents of glucan, xylan, extractives, acetyl group, and lignin are shown in Table 1. The composition of EFB fibers is important in calculating the conversion yield of various products from EFB. The as-received EFB fibers and ball-milled EFB fibers could be converted into LA in the presence of 2 mM

Pb(II) at high temperature (210 °C) for 2 h. The yield of LA from raw EFB fibers was 24.8%, while ball-milled EFB fibers yielded 42.5%. Ball milling reduced the physical size and crystallinity of the fibers (Fig. 1), enhancing the hydrolysis conversion process. The yield of LA obtained was higher because ball-milled EFB fibers are easier to be hydrolyzed into monomeric sugars compared with raw EFB fibers because of its amorphous structure. This is corroborated in our previous study, in which ball-milled EFB fibers increased the yield of conversion products significantly (Chin *et al.* 2015).

Table 1. Chemical Components of Oil Palm EFB Fibers

Components	Mass fraction in percentage (%)
Lignin (acid-soluble)	5.78 ± 0.02
Lignin (acid-insoluble)	18.68 ± 0.19
Glucan	39.94 ± 0.96
Xylan	27.06 ± 0.63
Ash	1.57 ± 0.20
Extractives	9.49 ± 0.51
Acetyl content	8.32 ± 0.24

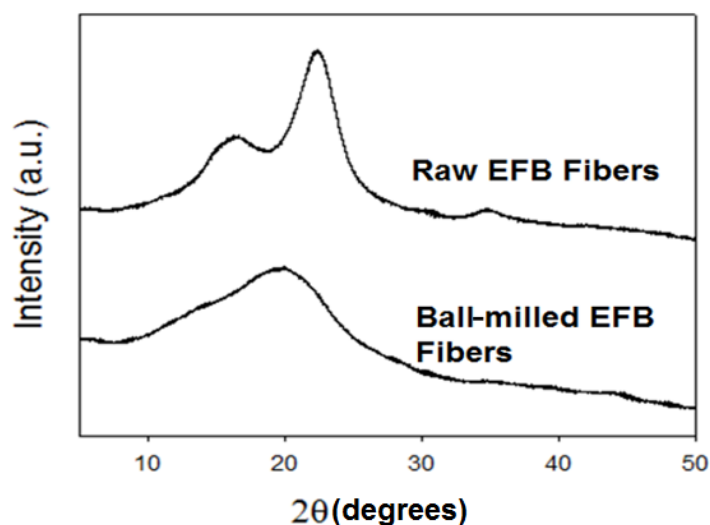


Fig. 1. XRD patterns of raw EFB fibers and ball-milled EFB fibers

The Effect of Pb(II) Ion Catalyst on the Decomposition of EFB Fibers into LA (Reaction Pathway)

In this study, the hydrothermal process is important, where hydrolysis at high temperature depolymerizes the cellulose and hemicelluloses of the EFB fibers into monosaccharides. The release of monosaccharides, such as glucose and xylose, serves as a starting point for further conversion into fine chemicals such as LA. When the reaction temperature is higher than 150 °C, the ionization constant (k_w) of water increases, weakening the hydrogen bonding of water molecules and enhancing the formation of hydronium ions (H_3O^+) (Hoekman *et al.* 2011; Xiao *et al.* 2012). H_3O^+ can act as a catalyst for the cleavage of β -(1,4) glycosidic linkages at C1 and C4 of glucan and hydrolyzes β -(1,4)-D-xylopyranose and O-acetylated xylopyranose of xylan to xylose and acetic acid, respectively (Ruiz *et al.* 2013; Chan *et al.* 2015).

Experimental runs were performed to verify the catalytic effect of Pb(II) ions in the production of LA from EFB fibers (0 mM and 2 mM Pb(II), 210 °C for 4 h). As shown in Fig. 2, in the absence of Pb(II), both glucose and xylose were degraded into products such as 5-HMF (21.3%), furfural (15.8%), and levulinic acid (3.1%). On the other hand, in the presence of Pb(II), the reaction favored the formation of LA, with 41.9% LA and relatively low yields of 5-HMF (0.22%) and furfural (1.9%). The presence of Pb(II) ions had a positive effect on the formation of LA from EFB fibers.

EFB fibers consist primarily of polysaccharides incorporating two main types of sugars (glucose and xylose). To determine whether glucose and xylose are the key starting sugar monomers in the production of LA, a hydrothermal reaction was performed using 1 g/L of glucose and 1 g/L of xylose (reaction conditions: 210 °C, 2 h) separately in the absence and presence of Pb(II) (Fig. 3 a-c). In the absence of Pb(II) ions, the main degradation products obtained from glucose and xylose were 5-HMF (21.44%) and furfural (32.52%), respectively. A trace amount of LA was found in both reactions (1.15% and 1.28%) (Fig. 3a and b (0 mM Pb(II))). However, in the presence of Pb(II), it was found that the yield of 5-HMF and furfural were extremely low, *i.e.*, 0.16% and 0.39%, respectively, and the yield of LA obtained from both glucose and xylose increased greatly, to 28.11% and 55.29%, respectively (Fig. 3a and b (2 mM Pb(II))). Figure 3c shows the color changed of the hydrolysate after the hydrothermal reaction. For glucose and xylose, after the hydrothermal reaction (0 mM Pb(II)), the color changed from transparent into yellowish brown. This was mostly due to the formation of degradation products such as 5-HMF and furfural. In the presence of 2 mM Pb(II), no changes in color were observed. This can be correlated with the result obtained above; in the presence of Pb(II), the yields of both 5-HMF and furfural were low.

In the absence of Pb(II), after the hydrothermal reaction, some glucose could still be found in the hydrolysate. However, no fructose was observed after the reaction, mostly because of the rapid transformation into LA at high temperature (Fig. 3a). Meanwhile, for the reaction carried out using xylose as the starting component, no xylose was observed after the reaction (Fig. 3b). In addition, as shown in Fig. 3, the yield of LA from glucose was lower than that from xylose. This may be due to its chemical structure, where C5 sugars degrade more quickly into other products compared with C6 sugars. This makes EFB fibers an attractive starting material for LA production because of their high xylan content, where hemicellulose (*i.e.*, xylose) is much easier to hydrolyze because of its heterogeneous structure and lower degree of polymerization.

Figure 4 shows the preferred reaction pathway for the conversion of EFB fibers into different products in the absence and presence of Pb(II). In the absence of Pb(II), the reaction pathways will be favorable toward pathway (a). An auto-hydrolysis process occurs, leading to the dehydration of both xylose and glucose into furfural and 5-HMF, humic products. As the reaction time is extended, furfural will be rehydrated into some degradation products. 5-HMF might be further rehydrated into levulinic acid and formic acid (Vegas *et al.* 2008). Formation of humic products or unwanted side reactions might occur at the same time. In the presence of Pb(II), the reaction pathway switches from pathway (a) to (b). The glucose-based route incorporates glycolysis of glucose, which involves isomerization to fructose (Eriksen *et al.* 1998). The introduction of Pb(II) results in the selective cleavage of the C-C bond in C3-C4 of fructose and C2-C3 bond in xylose into trioses (dihydroxyacetone and glyceraldehyde), followed by the selective conversion of trioses (retro-aldol condensation) and dehydration of pyruvaldehyde into LA (Yu *et al.* 2008; Wang *et al.* 2013).

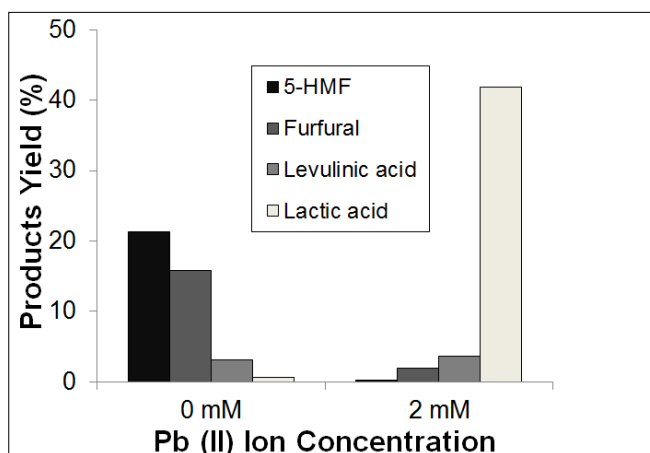


Fig. 2. Conversion products of EFB fibers in the absence (0 mM) and presence (2 mM) of Pb(II). Reaction conditions: 210 °C for 4 h

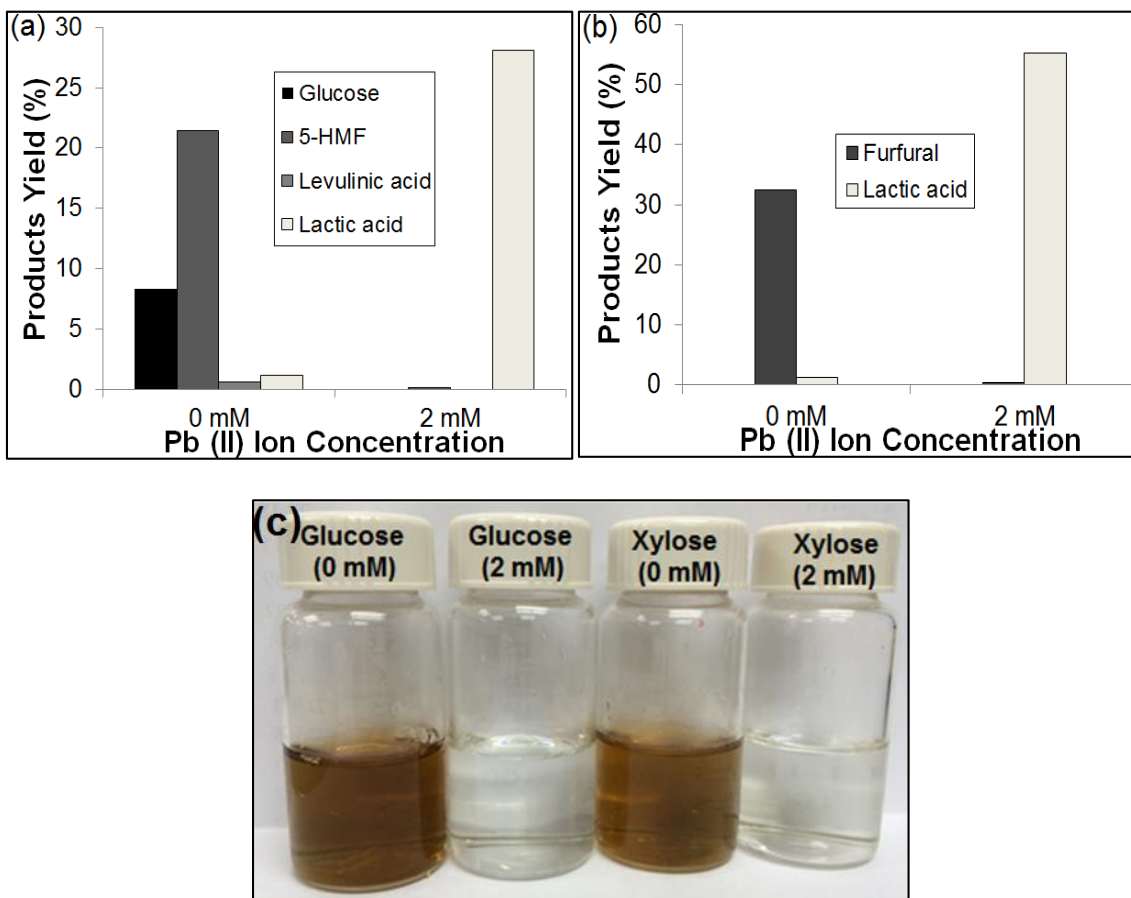


Fig. 3. (a) Conversion of glucose to lactic acid in the absence and presence of Pb(II); (b) conversion of xylose to lactic acid in the absence and presence of Pb(II); and (c) color difference between hydrolysates. Reaction conditions: 210 °C for 2 h

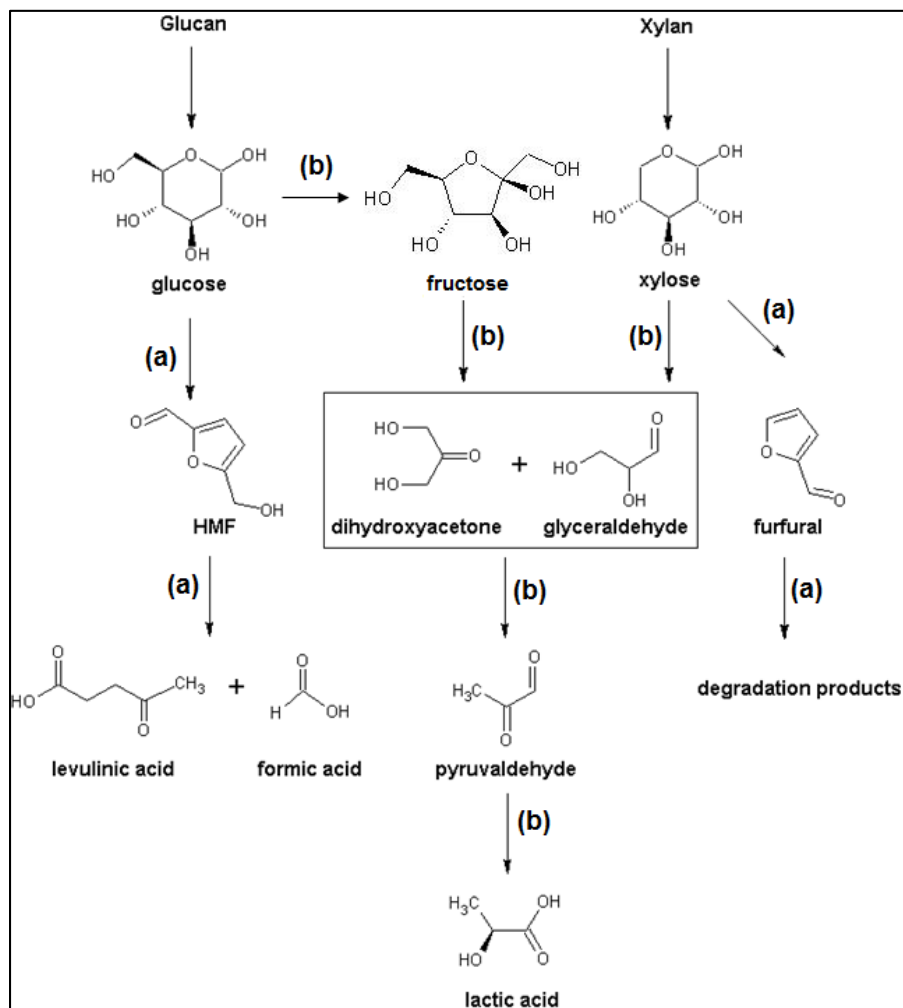


Fig. 4. Reaction mechanisms for conversion of EFB fibers into lactic acid in the (a) absence and (b) presence of Pb(II) ions

Effect of Temperature and Pb(II) Ion Concentration on the Production of Lactic Acid and Acetic Acid from EFB Fibers

The yield of LA obtained from EFB fibers in the presence of Pb(II) ions (0 to 14 mM) under hydrothermal conditions at various temperatures is presented in Fig. 5a. For reactions that were carried out at 170 and 190 °C, the LA yield increased consistently with increases in the reaction's severity (meaning higher temperature and higher Pb(II) ion concentration). Increasing concentrations of Pb(II) greatly enhanced the yield of LA, especially at lower reaction temperature (< 190 °C). Higher reaction temperatures promote the release of H_3O^+ ions, which subsequently attack the hydrogen bond network among hemicelluloses, cellulose, and lignin, making the cellulose within the EFB fibers more accessible. It was observed that at higher reaction temperature, the concentration of Pb(II) required can be decreased to achieve a high LA yield. For instance, the maximum yield of LA obtained at 170 °C was 23.14% using 14 mM Pb(II), whereas 46.5% LA could be obtained with only 2 mM Pb(II) at 230 °C. Higher reaction temperatures enhanced the cleavage of β -glycosidic bonds in β -(1,4)-D-glucopyranose, β -(1,4)-D-xylopyranose, and O-acetylated xylopyranose into glucose and xylose. Therefore, the LA yield for the reactions carried out at 170 and 190 °C was much lower than that at 210 and 230 °C because

of the slow release of glucose from the EFB fibers. It was also observed that at 230 °C, higher concentrations of Pb(II) resulted in the reduction of LA yield, which could be due to the degradation of LA into other, simpler products. It was also found that the fructose and xylose peaks overlapped each other in HPLC analysis. The elution times of these compounds are at 12.15 min (xylose) and 12.24 min (fructose). Therefore, the yield of fructose and xylose cannot be determined accurately and is not reported in this study.

Figure 6 shows the yields of glucose, 5-HMF, and furfural obtained from the hydrothermal processing of EFB fibers at various temperatures and Pb(II) concentrations (170 to 230 °C, 0 to 14 mM Pb(II)). All reactions were carried out for 4 h. In the absence of Pb(II) (0 mM), the yield of 5-HMF was higher than that with Pb(II) (Fig. 6b). As shown in Fig. 6a, for reactions that were carried out in the absence of Pb(II), glucose could be observed at 170 °C (1.86%) and 190 °C (20.43%). The rate of formation of glucose from glucan increased as the temperature increased; so did the rate of degradation of glucose. At higher reaction temperatures, *i.e.*, 210 and 230 °C, no glucose could be observed. The concentration of 5-HMF increased as the reaction temperature increased (170 to 210 °C). The highest yield of 5-HMF (21.32%) was achieved at 210 °C. This can be correlated with the yield of glucose and its subsequent degradation into 5-HMF. For the reaction at 230 °C, the yield of formation of 5-HMF was low. This is because, at higher reaction temperature, 5-HMF may be further degraded into levulinic acid and other degradation products (Chin *et al.* 2014).

Furfural is the main dehydration product of xylose (Fig. 6c). The yield of furfural followed the same trend as 5-HMF (Fig. 6b). The highest yield of furfural (27.14%) was achieved at 190 °C. Compared with 5-HMF, the maximum yield of furfural could be achieved at lower temperatures. This is because degradation of hemicellulose is easier than that of cellulose (Mou *et al.* 2013). Conversely, for reactions that were carried out in the presence of Pb(II), the yield of 5-HMF decreased greatly (Fig. 6c). The yield of LA also increased (Fig. 5a). This can be attributed to the fact that in the presence of Pb(II), the reaction process will shift from dehydration of sugars (glucose and xylose), yielding 5-HMF or furfural, into retro-aldol fragmentation of sugars (glucose and xylose), yielding LA (Wang *et al.* 2013).

Conversion of biomass into chemicals is very complicated and usually involves many competing and reversible reactions (Yu *et al.* 2008). Therefore, some low-molecular weight carboxylic acids, such as formic acid, levulinic acid, and acetic acid, can be found in the catalytic hydrothermal process. Formic acid and levulinic acid were generated from the rehydration of 5-HMF and furfural (Girisuta *et al.* 2013). The yields of formic and levulinic acids were low and are not the focus in this study; therefore, they are not reported.

Acetic acid is primarily generated from the hydrolysis of the acetyl groups present in the hemicellulosic heteropolymer (González-Muñoz *et al.* 2013). Some hemicellulosic monomers, such as xylose, are linked to acetyl groups, which can be hydrolyzed into acetic acid. Previous work by the authors (hydrolysis of EFB fibers *via* diluted acid) confirmed that acetic acid concentration increases until a constant value is attained, and the decomposition of acetic acid was not observed (Chin *et al.* 2014). This is consistent with previous reports using other lignocellulosic materials (Téllez-Luis *et al.* 2002; Guerra-Rodríguez *et al.* 2012). The yield of acetic acid is dependent on the number of acetyl groups present in the EFB fibers. Additionally, from Table 1, the acetyl content in the EFB fibers was approximately 8.34%. For a typical experimental run, 0.1 g of EFB fibers was mixed with 20 mL of Pb(II) aqueous solution. Therefore, it is estimated that approximately 0.42 g/L of acetic acid can be produced from the total acetyl content in the EFB fibers. As shown

in Fig. 5b, at reaction temperatures of 170 and 190 °C, the obtained acetic acid yield was from 0.35 to 0.45 g/L. A slight increase in the yield was obtained as the concentration of Pb(II) increased. However, the increment was not pronounced. It is believed that the acetic acid was generated from the hydrolysis of the acetyl groups in EFB fibers. At higher reaction temperatures (210 and 230 °C), the increase in the amount of acetic acid produced was higher as the concentration of Pb(II) increased. It was also observed that the yield of acetic acid exceeded the amount of acetyl groups of the EFB fibers. For example, at 230 °C with 14 mM Pb(II) (Fig. 5b), the acetic acid obtained was 0.8 g/L (16%). This could be attributed to the degradation of other products in the hydrolysate.

As the LA yield decreased, the yield of acetic acid increased (Fig. 5a and b). Therefore, it was speculated that the increase in acetic acid yield primarily comes from the degradation of LA. Increasing the temperature and concentration of Pb(II) would enhance the degradation of LA. To confirm this, a series of experiments was performed using LA (1 g/L) as the reactant (purity > 99.5%) in the absence (0 mM) and presence (2, 4, and 7 mM) of Pb(II) ions under various reaction times at 210 °C (Fig. 7).

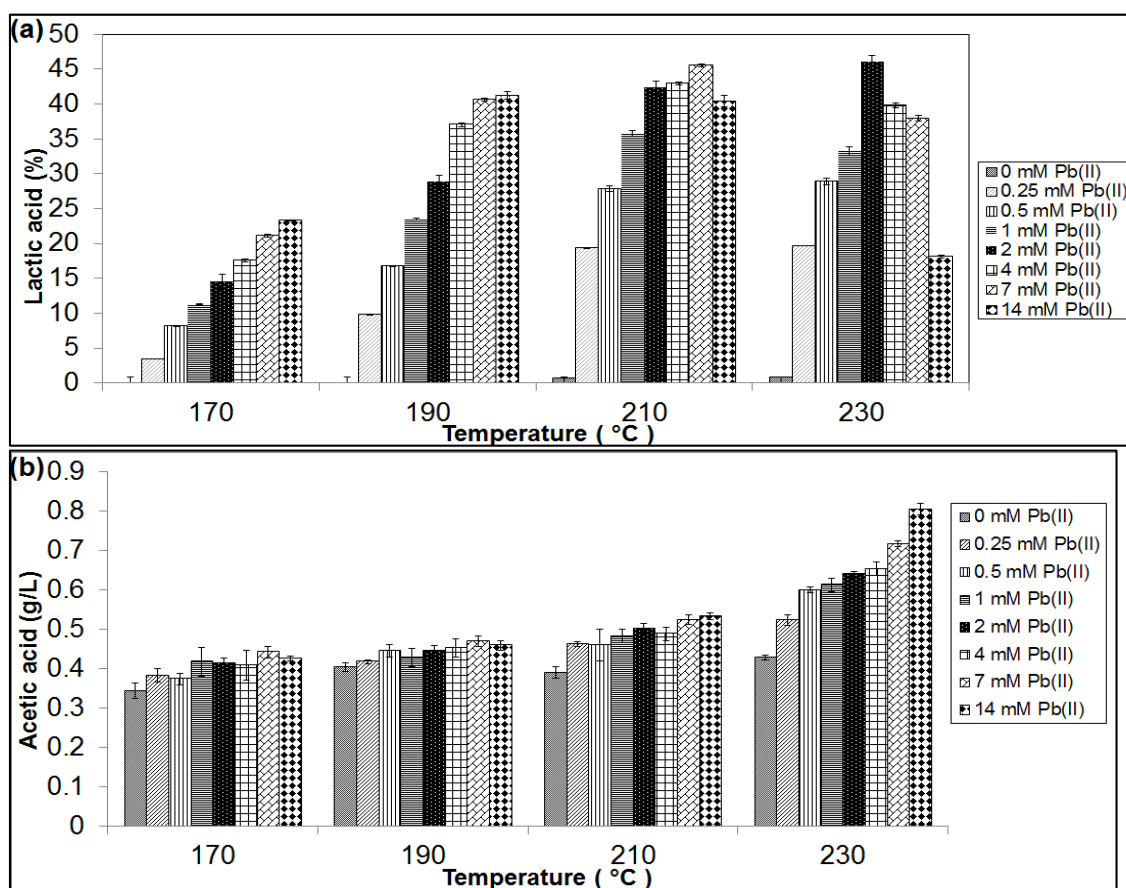


Fig. 5. Effects of reaction temperature and concentration of Pb(II) on the production of (a) lactic acid from EFB fibers and (b) acetic acid from EFB fibers

At high reaction temperature (210 °C), in the absence of Pb(II), it was observed that the hydrothermal process itself resulted in the degradation of LA (1 g/L to 0.91 g/L), concurrently producing small amounts of acetic acid. In the presence of Pb(II) ions, the degradation of LA became more pronounced (from 0.94 g/L to 0.78 g/L) as the

concentration of Pb(II) was increased from 2 to 7 mM. This shows that higher Pb(II) concentration will enhance the degradation of LA. Two reactions were carried out using 2 mM Pb(II) for 2 and 4 h. Initially, 1 g/L of LA was degraded to 0.94 and 0.42 g/L, respectively.

Longer reaction times will further enhance the degradation of LA (Fig. 7), while at the same time, an increase in acetic acid can be observed. On the other hand, it was observed that LA was degraded not only into acetic acid but also into other unidentified products. Oxidation processes may occur during the reaction, which can result in the degradation of LA into acetic acid, formic acid, or carbon dioxide (Yang *et al.* 2015). This also correlates with the results shown in Fig. 5a. As the reaction temperature and Pb(II) concentration increase, the production of LA will be enhanced and more LA will be degraded into acetic acid and other unidentified products.

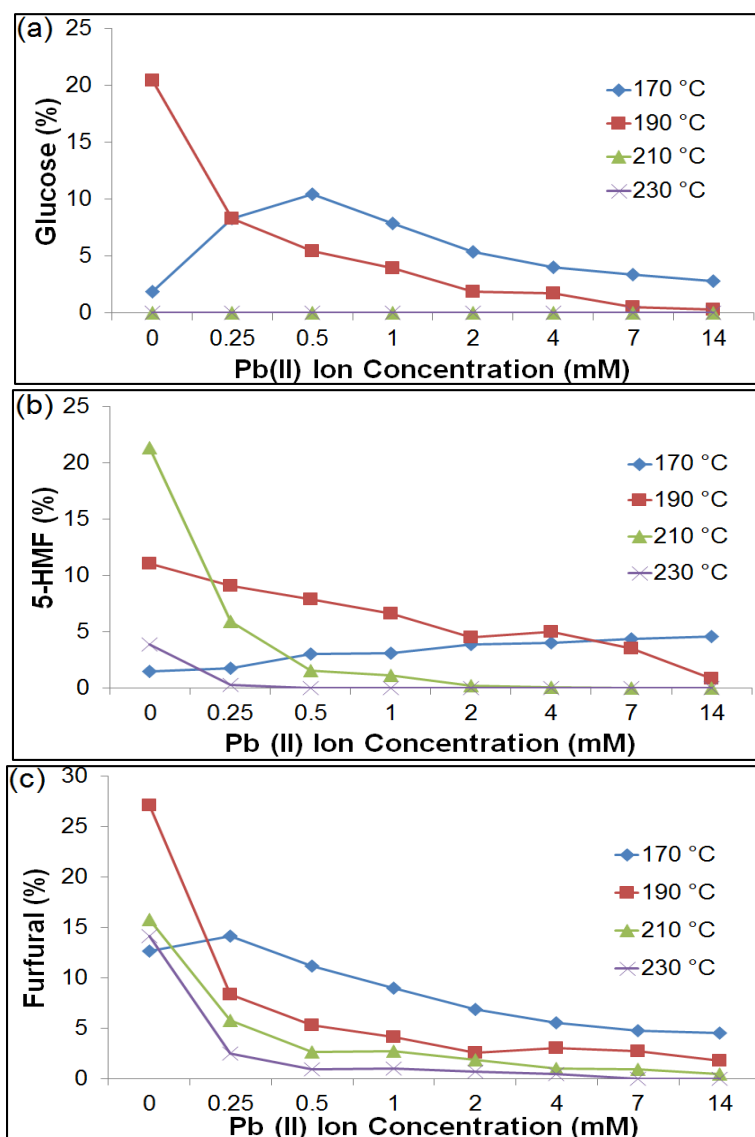


Fig. 6. Effects of reaction temperature and concentration of Pb(II) on the (a) formation of glucose from EFB fibers, (b) formation of 5-HMF from EFB fibers, and (c) formation of furfural from EFB fibers

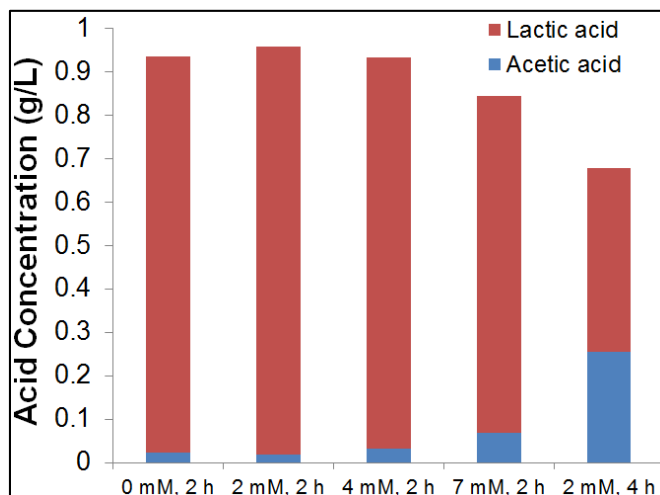


Fig. 7. Effect of concentration of Pb(II) ions and reaction time on the degradation of lactic acid

Effect of Reaction Time on the Production of Lactic Acid from EFB Fibers

Figure 8 shows the LA yield obtained from the hydrothermal reactions of EFB fibers carried out at 210 °C using two concentrations of Pb(II). For reactions that were carried out with 2 mM Pb(II), the highest yield of LA (43.57%) was achieved at 180 min. For reaction times from 0 to 60 min, the initial rate of reaction was high and the LA yield increased steeply. As the reaction time increased (> 60 min), the rate of formation of LA started to slow. Additionally, the LA yield decreased for reaction times longer than 180 min, which can be attributed to the degradation of LA. Further reaction time would enhance the degradation of LA, giving a lower yield of LA.

For reactions that were carried out using 7 mM Pb(II), the rate of formation of LA was higher than that of 2 mM Pb(II). Under the condition of 120 min reaction time and 7 mM Pb(II) ions, highest yield of LA (46.34%) can be achieved. Therefore, the time taken to achieve the maximum yield is highly dependent on the concentration of Pb(II) ions. It was observed that the rate of formation of LA using 7 mM Pb(II) was higher compared with that using 2 mM Pb(II). A higher concentration of Pb(II) increases the reaction rate and favors the formation of LA.

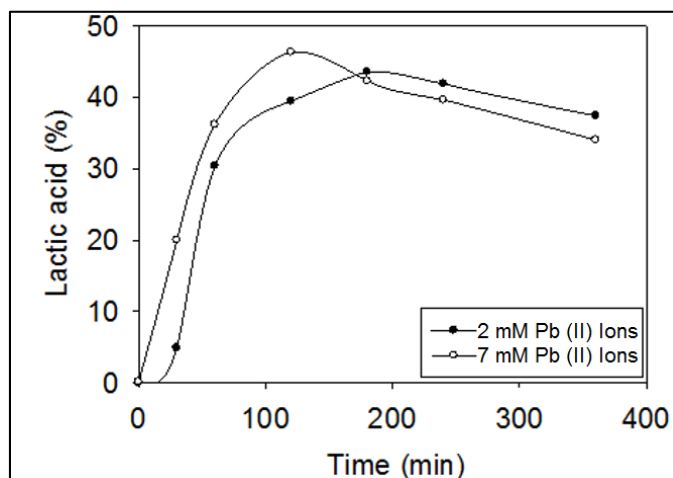


Fig. 8. Effect of reaction time on the production of lactic acid from EFB fibers (210 °C)

Experimental Design and Statistical Analysis

Response surface methodology (RSM) (central composite design) was performed to further understand and verify the effect of reaction time, Pb(II) concentration, and the interaction between these two factors on the production of LA from EFB fibers. The reaction temperature was fixed at 210 °C. This temperature was chosen because higher temperatures had adverse effects on the yield of LA, *i.e.*, enhancing unwanted side reactions instead of boosting the yield of LA.

A two-level full factorial design (2²) was applied in this study with two factors: X₁ (reaction time) and X₂ (Pb(II) ion concentration). The concentration of Pb(II) was expressed in log scale for better fit of the experimental model. Each factor was tested at three levels, as shown in Table 2. A total of 10 runs of experiments were carried out.

Table 2. Parameter Levels for the Two Factors in the Production of Lactic Acid from EFB Fibers

Factor	Symbol	Level		
	Coded	-1	0	1
Reaction time (h)	X ₁	1	3	5
Log Pb(II) ion concentration (mM)	X ₂	0.54	0.85	1.15

A second-order polynomial model for the predicted response of LA yield (Y) was then developed. This polynomial equation describes the relationship between the independent variables and the response variables:

$$Y = 41.98887 + 0.737457X_1 + 0.302812X_2 - 4.14075X_1^2 - 0.94417X_2^2 - 4.45017X_1X_2 \quad (2)$$

The fitted model accounted for over 94.78% of the variation in the production of LA from EFB fibers, and the adjusted R² was 88.26%. Only 5.22% of the total variability was not explained in the regression models. Both coefficients of determination (R² and adjusted R²) demonstrate the agreement between the experimental and predicted yield of LA. The analysis of variance (ANOVA) with low probability (Prob>F) 0.0113 shows that the fitted model was highly significant. The coefficients of Eq. 2 are shown in Table 3. The estimated parameters show the coefficients and significance of the linear, cross product, and quadratic terms on each response.

In Table 3, the absolute magnitudes in relation to the statistical significance (p-value of 0.05) are shown. The conversion of EFB fibers to LA was significantly affected by the cross product of Pb(II), concentration × time, and the quadratic effect of time. This means that the production of LA from EFB fibers was directly related to the cross effect of these two factors. The quadratic effect of time was significant in this model. This means that longer reaction time might have an adverse effect on the yield of LA, where LA might be degraded, forming humic products and undergoing unwanted side reactions at the same time. The effect of Pb(II) concentration alone was not significant in the production of LA. This can be further demonstrated in Fig. 9, showing the desirability profile of this model. The yield of LA varied little as the concentration of Pb(II) increased, remaining at approximately 40%. Figure 9 shows that the solution of this model was a saddle point, where the predicted yield of LA was 42.01%. Wang *et al.* (2013) observed the same phenomenon, in which longer reaction time and higher Pb(II) concentration can no longer

enhance the formation of LA. They performed the conversion of microcrystalline cellulose into LA in the presence of Pb(II) and found that further increases in the concentration of Pb(II) will only slightly increase the yield of LA, which plateaued at ~70%. Hence, the yield of LA is highly dependent on the experimental conditions. For instance, experimental conditions are more favorable when using lower concentrations of Pb(II) ions. Therefore, longer reaction time is required and *vice versa*. However, there is no point in using higher concentrations of Pb(II) because the LA yield varied little as the concentration of Pb(II) was further increased.

It can be seen that the conversion of EFB fibers into LA is very complex and the yield of LA attained fell between 40% and 46%. Some competitive side reactions might occur alongside this reaction because of the complex components in EFB fibers that hinder the conversion into LA. Lignin, extractives, or ash may also contribute to the yield of LA. To further improve the yield of LA, removal of lignin and extractives may help. Furthermore, it is well known that the separation of LA from aqueous solution is very complex, as it contains by-products such as sugars, organic acids, and some degradation products. Therefore, the product selectivity should be further improved to maximize yield and minimize the formation of degradation products. Further improvement in the LA yield can be expected through two-step reactions, where in the first step, xylan and glucan are both converted into xylose and glucose before continuing with the conversion into LA.

Table 3. Significance of Regression Coefficient of Lactic Acid Yield

Parameter estimates				
Variables	Regression coefficient	Std. error	t value	Significance level (p-value)
Intercept	41.9889	0.7978	52.6	<.0001*
X ₁	0.7376	0.5450	1.35	0.2474
X ₂	0.3028	0.5450	0.56	0.6081
X ₁ X ₂	-4.4502	0.6674	-6.67	0.0026*
X ₁ ²	-4.1408	0.8739	-4.74	0.0090*
X ₂ ²	-0.9442	0.8739	-1.08	0.3408

*Significant variable

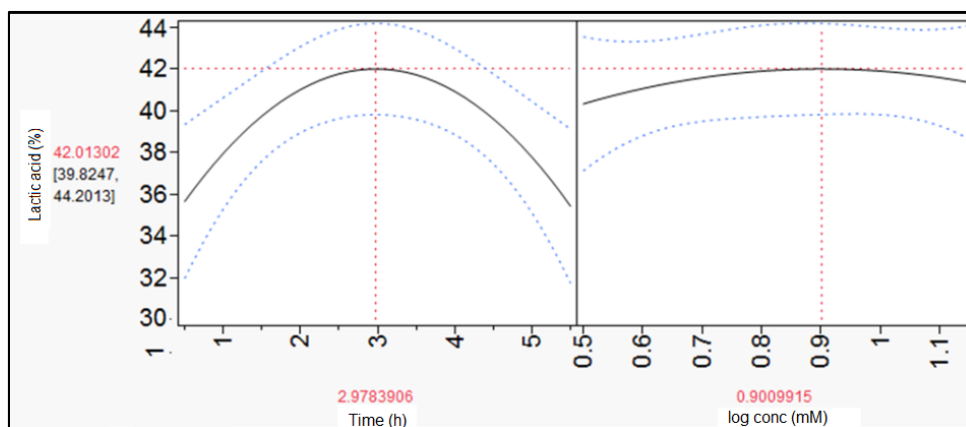


Fig. 9. Desirability profile of lactic acid yield

The use of Pb(II) as a catalyst is one of the main concerns in the conversion of EFB fibers to LA because of its toxicity. The separation and recovery of Pb(II) from the catalytic system should be considered before practical application. It was reported by Wang *et al.*

(2013) that Pb(II) in the reaction solution could be simply recovered using a cation exchange resin (Amberlite IR-120 resin). Thus, using this available technique, the risk of using Pb(II) as a catalyst can be reduced. In addition, a more effective system may be developed to expand the practical usability and efficiency of this catalytic system.

CONCLUSIONS

1. A direct hydrothermal transformation of LA (> 46%) from EFB fibers using Pb(II) ions as a catalyst was demonstrated.
2. The yield of LA from EFB fibers is highly dependent on the experimental conditions, where higher concentrations of Pb(II) will require shorter reaction time to obtain the maximum yield and *vice versa*.
3. Results obtained in this work can provide a better understanding of the formation mechanism of LA from EFB fibers using metal catalysts.
4. EFB fibers have great potential use as a raw material for LA production, and the results obtained in this current work can inspire further design of catalytic systems.

ACKNOWLEDGMENTS

The authors acknowledge Universiti Kebangsaan Malaysia for the financial support *via* research grants DIP-2014-013.

REFERENCES CITED

- Chan, C. H., Chia, C. H., Zakaria, S., Sajab, M. S., and Chin, S. X. (2015). "Cellulose nanofibrils: A rapid adsorbent for the removal of methylene blue," *RSC Adv.* 5(24), 18204-18212. DOI: 10.1039/C4RA15754K
- Chin, S. X., Chia, C. H., Fang, Z., Zakaria, S., Li, X. K., and Zhang, F. (2014). "A kinetic study on acid hydrolysis of oil palm empty fruit bunch fibers using a microwave reactor system," *Energy Fuels* 28(4), 2589-2597. DOI: 10.1021/ef402468z
- Chin, S. X., Chia, C. H., Zakaria, S., Fang, Z., and Ahmad, S. (2015). "Ball milling pretreatment and diluted acid hydrolysis of oil palm empty fruit bunch (EFB) fibres for the production of levulinic acid," *J. Taiwan Inst. Chem. Eng.* 52, 85-92. DOI: 10.1016/j.jtice.2015.01.028
- de Clippel, F., Dusselier, M., Van Rompaey, R., Vanelderden, P., Dijkmans, J., Makshina, E., Giebeler, L., Oswald, S., Baron, G. V., Denayer, J. F. M., *et al.* (2012). "Fast and selective sugar conversion to alkyl lactate and lactic acid with bifunctional carbon-silica catalysts," *J. Am. Chem. Soc.* 134(24), 10089-10101. DOI: 10.1021/ja301678w
- Deuss, P. J., Barta, K., and de Vries, J. G. (2014). "Homogeneous catalysis for the conversion of biomass and biomass-derived platform chemicals," *Catal. Sci. Tech.* 4(5), 1174-1196. DOI: 10.1039/C3CY01058A

- Dusselier, M., Van Wouwe, P., Dewaele, A., Makshina, E., and Sels, B. F. (2013). "Lactic acid as a platform chemical in the biobased economy: The role of chemocatalysis," *Energ. Environ. Sci.* 6(5), 1415-1442. DOI: 10.1039/C3EE00069A
- Eriksen, J., Mønsted, O., and Mønsted, L. (1998). "Mechanism of lactic acid formation catalyzed by tetraamine rhodium(III) complexes," *Transit. Metal. Chem.* 23(6), 783-787. DOI: 10.1023/A:1006988916647
- Folkedahl, B. C., Snyder, A. C., Strege, J. R., and Bjorgaard, S. J. (2011). "Process development and demonstration of coal and biomass indirect liquefaction to synthetic iso-paraffinic kerosene," *Fuel Process. Technol.* 92(10), 1939-1945. DOI: 10.1016/j.fuproc.2011.05.013
- Girisuta, B., Dussan, K., Haverty, D., Leahy, J. J., and Hayes, M. H. B. (2013). "A kinetic study of acid catalysed hydrolysis of sugar cane bagasse to levulinic acid," *Chem. Eng. J.* 217, 61-70. DOI: 10.1016/j.cej.2012.11.094
- González-Muñoz, M. J., Rivas, S., Santos, V., and Parajó, J. C. (2013). "Aqueous processing of *Pinus pinaster* wood: Kinetics of polysaccharide breakdown," *Chem. Eng. J.* 231, 380-387. DOI: 10.1016/j.cej.2013.07.041
- Guerra-Rodríguez, E., Portilla-Rivera, O. M., Jarquín-Enríquez, L., Ramírez, J. A., and Vázquez, M. (2012). "Acid hydrolysis of wheat straw: A kinetic study," *Biomass Bioenerg.* 36, 346-355. DOI: 10.1016/j.biombioe.2011.11.005
- Hayashi, Y., and Sasaki, Y. (2005). "Tin-catalyzed conversion of trioses to alkyl lactates in alcohol solution," *Chem. Commun.* 21, 2716-2718. DOI: 10.1039/B501964H
- Hoekman, S. K., Broch, A., and Robbins, C. (2011). "Hydrothermal carbonization of lignocellulosic biomass," *Energy Fuels* 25(4), 1802-1810. DOI: 10.1021/ef101745n
- Huber, G.W., Iborra, S., and Corma, A. (2006). "Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering," *Chem Rev* 106 (9):4044-4098. DOI: 10.1021/cr068360d
- Lin, Y., and Tanaka, S. (2006). "Ethanol fermentation from biomass resources: Current state and prospects," *Appl. Microbiol. Biotechnol.* 69(6), 627-642. DOI: 10.1007/s00253-005-0229-x
- Ludin, N. A., Bakri, M. A. M., Kamaruddin, N., Sopian, K., Deraman, M. S., Hamid, N. H., Asim, N., and Othman, M. Y. (2014). "Malaysian oil palm plantation sector: Exploiting renewable energy toward sustainability production," *J. Clean Prod.* 65(6), 9-15. DOI: 10.1007/s00253-005-0229-x
- Mou, H.-Y., Orblin, E., Kruus, K., and Fardim, P. (2013). "Topochemical pretreatment of wood biomass to enhance enzymatic hydrolysis of polysaccharides to sugars," *Bioresour. Technol.* 142 (0), 540-545. DOI: 10.1016/j.biortech.2013.05.046
- National Biomass Strategy. (2013). *National Biomass Strategy 2020: New Wealth Creation for Malaysia's Biomass Industry*, <http://www.innovation.my/pdf/1mbas/Biomass20Strategy2013.pdf>
- Orozco, A. M., Al-Muhtaseb, A. a. H., Rooney, D., Walker, G. M., and Ahmad, M. N. M. (2013). "Hydrolysis characteristics and kinetics of waste hay biomass as a potential energy crop for fermentable sugars production using autoclave Parr reactor system," *Ind. Crop. Prod.* 44, 1-10. DOI: 10.1016/j.indcrop.2012.10.018
- Peng, L., Lin, L., Zhang, J., Zhuang, J., Zhang, B., and Gong, Y. (2010). "Catalytic conversion of cellulose to levulinic acid by metal chlorides," *Molecules* 15(8), 5258-5272. DOI: 10.3390/molecules15085258
- Ruiz, H. A., Rodríguez-Jasso, R. M., Fernandes, B. D., Vicente, A. A., and Teixeira, J. A. (2013). "Hydrothermal processing, as an alternative for upgrading agriculture

- residues and marine biomass according to the biorefinery concept: A review,” *Renew. Sust. Energ. Rev.* 21, 35-51. DOI: 10.1016/j.rser.2012.11.069
- Sitompul, J. P., Simangunsong, R. F., Asrizal, A. A., Alisyahbana, H., Lee, H. W., and Rasrendra, C. B. (2014). “Catalytic conversion of empty fruit bunch of palm oil for producing lactic acid,” *Procedia Chem.* 9, 88-93. DOI: 10.1016/j.proche.2014.05.011
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2010). “Determination of structural carbohydrates and lignin in biomass,” NREL/TP-510-42618, National Renewable Energy Laboratory, Golden, CO.
- Sluiter, A., Ruiz, R., Scarlata, C., Sluiter, J., and Templeton, D. (2008). “Determination of extractives in biomass,” NREL/TP-510-42619, National Renewable Energy Laboratory, Golden, CO.
- Téllez-Luis, S. J., Ramírez, J. A., and Vázquez, M. (2002). “Mathematical modelling of hemicellulosic sugar production from sorghum straw,” *J. Food Eng.* 52(3), 285-291. DOI: 10.1016/S0260-8774(01)00117-0
- Vegas, R., Kabel, M., Schols, H. A., Alonso, J. L., and Parajó, J. C. (2008). “Hydrothermal processing of rice husks: Effects of severity on product distribution,” *J. Chem. Technol. Biotechnol.* 83(7), 965-972. DOI: 10.1002/jctb.1896
- Wang, Y., Deng, W., Wang, B., Zhang, Q., Wan, X., Tang, Z., Wang, Y., Zhu, C., Cao, Z., Wang, G., and Wan, H. (2013). “Chemical synthesis of lactic acid from cellulose catalysed by lead(II) ions in water,” *Nat. Commun.* 4, 1-7. DOI:10.1038/ncomms3141
- Werpy, T., and Petersen, G. (2004). “Top value added chemicals from biomass: Volume I - Results of screening for potential candidates from sugars and synthesis gas”, <http://energy.gov/eere/bioenergy/downloads/top-value-added-chemicalsbiomass-volume-i-results-screening-potential>
- Xiao, L. P., Shi, Z. J., Xu, F., and Sun, R.C. (2012). “Hydrothermal carbonization of lignocellulosic biomass,” *Bioresour. Technol.* 118, 619-623. DOI: 10.1016/j.biortech.2012.05.060
- Yan, K., Yang, Y., Chai, J., and Lu, Y. (2015). “Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals,” *Appl. Catal. B: Environ.* 179, 292-304. DOI: 10.1016/j.apcatb.2015.04.030
- Yang, L., Su, J., Carl, S., Lynam, J. G., Yang, X., and Lin, H. (2015). “Catalytic conversion of hemicellulosic biomass to lactic acid in pH neutral aqueous phase media,” *Appl. Catal. B: Environ.* 162, 149-157. DOI: 10.1016/j.apcatb.2014.06.025
- Yu, Y., Lou, X., and Wu, H. (2008). “Some recent advances in hydrolysis of biomass in hot-compressed water and its comparisons with other hydrolysis methods,” *Energy Fuels* 22(1), 46-60. DOI: 10.1021/ef700292p

Article submitted: September 27, 2015; Peer review completed: December 2, 2015;
Revised version received and accepted: December 29, 2015; Published: January 19, 2016.
DOI: 10.15376/biores.11.1.2186-2201