



## Research paper

## An intensified reaction technology for high levulinic acid concentration from lignocellulosic biomass



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## ARTICLE INFO

## Article history:

Received 22 January 2016

Received in revised form

14 September 2016

Accepted 21 October 2016

## Keywords:

Levulinic acid

Lignocellulosic biomass

Eucalyptus wood

Xylose

Humins

## ABSTRACT

An intensified reaction technology was investigated to achieve high concentrations of levulinic acid (LA) from eucalyptus wood. In the new process, the woody biomass was first pretreated in mild conditions to hydrolyze hemicellulose and recover xylose. The pretreated wood with a high content of cellulose was further treated under relatively severe conditions to produce LA and formic acid. The reaction solution was reused in treatment of new batches of biomass, resulting in high concentrations of LA (105 g/L) and formic acid (39 g/L), respectively. The lignin and humins were recovered as solid byproducts, which had an estimated high heating value of 25–27 MJ/kg in comparison with 18 MJ/kg of original wood. In the sequential repeated batch reactions, however, the LA yield deteriorated batch by batch. It was found out that the old LA in the reaction solution inhibited formation of new LA from glucose. In addition, some LA at high concentrations was lost due to its interactions with other intermediates and byproducts.

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## 1. Introduction

Levulinic acid (LA) is considered as one of top twelve value-added chemicals derived from renewable biomass [1,2]. LA is currently used in a variety of applications including personal care products, adsorbents, lubricants, photography, and drug delivery systems [3–5]. As a promising building-block chemical, LA can also be used for production of various important chemicals such as succinic acid,  $\gamma$ -valerolactone, calcium levulinate, 1,4-butanediol, tetrahydrofuran, acrylic acid, and ethyl levulinate [5,6]. Under acid catalysis, hexoses such as fructose and glucose can be effectively converted into LA and formic acid in aqueous solution [1,2]. Lignocellulosic biomass, however, is a preferred feedstock for large scale production with the concerns on the process sustainability and economics. Various lignocellulosic biomass including pinus radiata, sugarcane bagasse, wheat straw and paddy straw have been investigated for LA production [7–9]. Biofine process is a well-known technology for large scale LA production from lignocellulose, in which sulfuric acid ( $H_2SO_4$ ) is used as the catalyst [10]. Lignocellulose primarily contains cellulose, hemicellulose and lignin [11], which have different fates in the reaction conditions of LA formation. Cellulose, a polymer of glucose, can be effectively

hydrolyzed and converted into LA and formic acid with glucose and 5-hydroxymethylfurfural (HMF) being the key intermediates [1,5,6]. In this route, cellulose is first hydrolyzed into glucose, followed by dehydration of glucose into HMF, and rehydration of HMF into LA and formic acid [12]. Hemicellulose, because of its branched and amorphous structure, is easily hydrolyzed and converted into C5 sugars (mainly xylose) and furfural [13,14]. Under the severe conditions for LA formation, however, furfural can further react with sugars to form humins, the dark-brownish solid byproducts [15,16]. The presence of hemicellulose in the reaction solution therefore not only fails in obtaining the values of C5 sugars and furfural, but also reduces the LA yield [17]. Unlike cellulose and hemicellulose, lignin is a phenolic polymer that requires much severe conditions for decomposition, even though part of lignin may be dissolved in the reaction solution as acid soluble lignin [18,19]. Obviously, an effective refining of lignocellulosic biomass needs full utilization of hemicellulose, cellulose and lignin according to their chemical and physical properties. One possible technology is to recover C5 sugars from hemicellulose under mild conditions and then produce LA under severe conditions from the cellulose of pretreated biomass. Lignin is recovered as the main component of the residual solids.

Lignocellulosic biomass is not soluble in an aqueous reaction solution and hence a mineral acid such as  $H_2SO_4$  and HCl is an effective homogenous proton catalyst that can penetrate into the heterogeneous matrix of biomass. The load ratio of biomass solid to aqueous solution, however, is limited to 10–20 wt%, resulting in a

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low nominal concentration of hexoses (50–100 g/L). Because of a moderate LA yield from hexoses, the final LA concentration of the reaction solution is quite low (20–40 g/L). Indeed, a yield of 50–60% of theoretical one (64.4 wt% of hexoses) was often considered as a high LA yield [20–22]. A low LA concentration would cause a high cost of LA separation in the downstream process. It is often found in chemical industry that the separation cost may account for 50% or more of the whole process [23,24].

Little work has been done in reaction intensification to achieve high LA concentrations (>100 g/L). More often than not a low LA concentration (<30 g/L) is reported in the literature as shown in Table S1. In this work, we first time investigated a highly intensified reaction technology to achieve a high LA concentration from eucalyptus wood. First, hemicellulose was removed from the wood biomass to recover xylose and equally important to increase the cellulose content of the pretreated biomass for LA formation. Second, the reaction solution including acid catalyst and LA were separated from the residual solids (primarily lignin and humins) via filtration and reused to treat a new batch of biomass. Theoretically, the sequential treatments can be repeated to obtain a very high LA concentration, but it was found out that the LA yield deteriorated batch by batch. Some factors that might cause the LA yield loss were investigated and discussed in this work.

## 2. Materials and methods

### 2.1. Materials

D-(+)-glucose (96%), levulinic acid (LA, 98%), 5-(Hydroxymethyl) furfural (HMF, 99%), xylose (99%) and furfural (99%) were obtained from Sigma-Aldrich (MO, USA). Eucalyptus wood chips were provided by a local farmer (Maui, Hawaii) and grounded into small pieces (<2 mm × 2 mm × 4 mm) before use. Table 1 gives the major components of eucalyptus wood.

### 2.2. Wood biomass pretreatment

Diluted H<sub>2</sub>SO<sub>4</sub> solutions (0.01–0.15 M) were used for pretreatment of eucalyptus wood (100 or 150 g/L) at 150–170 °C. Pre-determined amounts of wood chips were put in PTFE containers (20 mL) and sealed in stainless steel cylinders. They were heated in an air-circulated oven at pre-set temperatures. The reactor temperature reached the pre-set temperatures (±2 °C) in about 60 min. The holding time was started after 60 min heating and recorded thereafter. After reaction, the reactors were quickly cooled down under tap water. The products were separated into aqueous solution and solid residues (pretreated wood) with filtration under vacuum. The pretreated wood were recovered and washed with water on pre-dried and pre-weighted Whatman filter papers and dried to constant weight at 60 °C for measurement. The aqueous solutions including washing water were collected and diluted with water in 100 mL volumetric flasks.

To obtain a sufficient amount of pretreated wood for LA formation, eucalyptus wood (40 g wood in 400 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> solution) was pretreated in a 600 mL unstirred acid-resistant Alloy-20 autoclave (Parr Instrument Co., Ltd., USA) at 150 °C for a holding time of 20 min. After the pretreatment, the residual wood (about 70.5 wt% of original wood mass) was recovered with filtration. After washed with water and dried at 60 °C to constant weight, the pretreated wood was labeled as P-wood and stored in a desiccator for later use. The major components of P-wood can be found in Table 1.

### 2.3. Reactions for LA formation

The reactions in this work include one batch reaction and repeated batch reactions for reusing of the reaction solution. All one batch reactions were conducted in the 20 mL PTFE reactor at 170 °C in 0.2 M H<sub>2</sub>SO<sub>4</sub> solution if without special mention. The products separation was the same as the pretreatment process described above.

#### 2.3.1. Repeated batch reactions

The sequential repeated batch reaction for reusing of the reaction solution is shown in Fig. 1. All these reactions were conducted in a 180 mL pyro-beaker, which was put in a 600 mL unstirred Alloy-20 reactor. In the first batch of the reactions, 16 g eucalyptus wood (or 16 g P-wood or 8 g glucose) was mixed with 80 mL of 0.2 M H<sub>2</sub>SO<sub>4</sub> solution in the pyro-beaker. The pyro-beaker was covered by a polytetrafluoroethylene lid but not sealed tightly. About 30 mL of water was added outside of the pyro-beaker, which facilitated heating and equalized the vapor pressure inside and outside of the pyro-beaker. After N<sub>2</sub> flush, the reactor was heated from room temperature to 170 °C in about 50 min and maintained at 170 °C for 5 h. After the reaction, the reactor was cooled down slowly in air to room temperature in about 1 h. The temperature and pressure were recorded when gas samples were taken for composition analysis. The reaction solution was separated from the residual solids with filtration, and its volume loss during the operation was compensated with a water solution (3–15 mL) from solids washing. The reaction solution was then mixed with a new batch of biomass for a repeated reaction by following the same procedure above. This process was sequentially repeated till a desired LA concentration in the reaction solution was obtained.

### 2.4. Analysis and calculation

#### 2.4.1. Aqueous products

The reaction and washing solutions were collected and diluted to 100 mL. The water soluble products were analyzed with a high performance liquid chromatograph (HPLC, Shimadzu, Japan) equipped with a C6H10 column (Supelco, Sigma-Aldrich, St. Louis, MO) and a refractive index detector. The column was kept at 50 °C and eluted with deionized water (pH 2.0 with sulfuric acid) at

**Table 1**  
Composition of eucalyptus wood, pretreated wood (P-wood)<sup>a</sup>, and reaction derived residues from accumulated reaction.

	C (wt%)	H (wt%)	N (wt%)	O <sup>b</sup> (wt%)	Glucan <sup>c</sup> (wt%)	Xylan <sup>c</sup> (wt%)	Lignin <sup>c</sup> (wt%)	Moisture <sup>c</sup> (wt%)	Ash <sup>c</sup> (wt%)	HHV <sup>d</sup> (KJ/kg)
Eucalyptus wood	45.92	5.56	0.12	47.90	48.9	12.4	26.7	9.4	0.5	17.6
P-wood	47.81	5.64	0.10	45.95	63.8	0	34.6	0	0.5	18.6
P-wood residue from 1st reaction	66.82	5.19	0.11	27.48	0	0	–	0	0.4	26.6
P-wood residue from 2nd reaction	67.58	5.49	0.19	26.34	0	0	–	0	0.4	27.3
P-wood residue from 3rd reaction	63.82	5.05	0.11	30.62	0	0	–	0	0.4	25.1

<sup>a</sup> P-wood was obtained from a pretreatment condition of 0.1 M H<sub>2</sub>SO<sub>4</sub> at 150 °C for a holding time of 20 min in the 600 mL Parr reactor.

<sup>b</sup> The O content is measured by difference.

<sup>c</sup> It is measured according method NREL/TP-510-42618 [19], and the contents of glucan, xylan and lignin are based on the dry basis of the wood.

<sup>d</sup> HHV is calculated base on reference [21] and [22]: HHV (MJ·kg<sup>-1</sup>) = 0.3491C + 1.1783H + 0.1005S – 0.1034O – 0.0015N – 0.0211A.

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