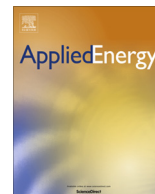




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# Intensified levulinic acid/ester production from cassava by one-pot cascade prehydrolysis and delignification

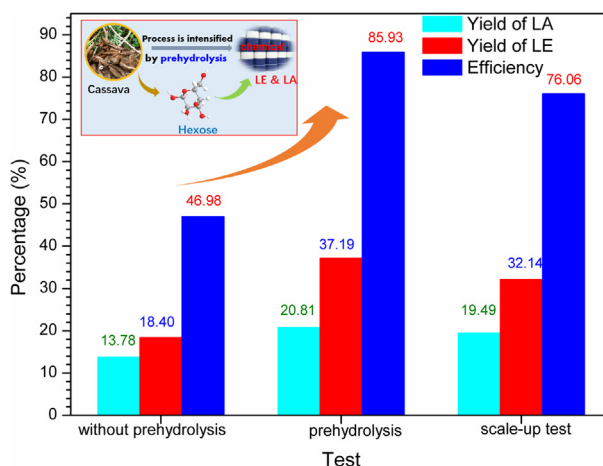
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## HIGHLIGHTS

- Prehydrolysis shows significant intensification effect on the cassava conversion.
- The process efficiency with prehydrolysis is almost twice of that without it.
- 60.36% levulinic acid/ester yield with 88.90% process efficiency can be obtained.
- Efficient lignin removal is positive for levulinic acid/ester formation.
- This process is robust for the scale-up test as well.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel and efficient process for levulinic acid/ester production from non-edible cassava is proposed via a one-pot cascade processes of prehydrolysis and delignification. The intensification effect of monosaccharide formation (prehydrolysis) and the solvent effect for delignification were investigated extensively. The influences of reaction conditions, such as, reaction temperature, time and catalyst concentration, were examined. The results show that prehydrolysis and delignification have significant promotional effects on levulinic acid/ester production. 60.36% levulinic acid/ester yield at a process efficiency of 88.90% can be obtained at 160 °C for 3.0 h when cassava is pretreated at 100 °C for 1.0 h. However, only 32.18% yield and 46.98% process efficiency are observed without prehydrolysis. Characterization of the starting feedstock and residues using compositional analysis, Fourier transform infrared spectroscopy, and elemental analysis demonstrate that efficient lignin removal has a positive influence for levulinic acid/ester formation. Moreover, this process is robust and suitable for scale-up, indicating that it has a great potential for industrial levulinic acid/ester production.

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## 1. Introduction

The efficient utilization of renewable lignocellulosic biomass has attracted significant attention during the last few decades, owing to the depletion of fossil fuels and increasingly serious

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environmental concerns [1–6]. Levulinic acid (LA) is one of the top twelve value-added platform chemicals from biomass and is a versatile building block for the production of numerous compounds and has potential as a fuel additive in its own right [7,8]. Furthermore, it is a good starting material for renewable jet-fuel production, via successive Aldol condensation and hydrogenation reactions [9,10]. Moreover, LA and its esters can be converted to a series of renewable chemicals such as, methyltetrahydrofuran and alkyl pentanoic esters (valeric biofuels) [9]. In particular, ethyl levulinate (LE) has found application in synthesizing  $\gamma$ -valerolactone, an attractive solvent and fuel additive, which is also a novel bio-diluent for biodiesel due to its high saturated fatty acid content [9,10]. Generally, LE comes from esterification of LA with the corresponding alcohol, promoted by acid catalysts. LA is produced from the dehydration of hexose (glucose and fructose), using acid catalysts, which occurs according to Fig. 1. Hexose dehydrates to 5-hydroxymethylfurfural (HMF), which is another key platform chemical from sustainable biomass, subsequent rehydration produces LA with equimolar amounts of formic acid [11,12]. An additional route to LA can be obtained from pentose (xylose, the major component of hemicellulose), via dehydration of xylose to furfural, which hydrogenates to furfuryl alcohol, followed by hydrolysis over acidic catalysts [11]. However, as is well known, the direct use of sugar as raw material is economically unfeasible due to sugar production having a relatively high energy-cost. Carbohydrates such as starch, cellulose and lignocellulosic biomass are promising raw materials for LA production [13–19]. For example, with sulfonated hyperbranched polymer catalysts, 31.1% process efficiency was obtained with starch under hydrothermal conditions at 165 °C for 5.0 h [14]. Significant process intensification was observed when starch was converted in methanol, 48.7% methyl levulinate yield was found in the presence of H<sub>2</sub>SO<sub>4</sub>, which could be explained by the synergistic effect between carbohydrate depolymerization and LA esterification [15]. As described above, numerous processes can effectively convert carbohydrate to LA and its esters, however, their energy efficiencies require further improvement.

To further promote process efficiency, Fitzpatrick patented a continuous process for promoting LA production [20]. In which, carbohydrates are hydrolyzed in a single reactor for the formation of HMF and then hydrolyzed to LA in a second reactor, under optimized conditions, a process efficiency of 70% could be obtained. However, large energy consumption is needed for HMF production and separation, due to its high boiling point. Furthermore, the application of a two-step operation increases economic equipment costs and makes the process more laborious, while the formation of humins during HMF hydrolysis is a significant challenge. Previous process analysis has demonstrated that this hydrolysis step is limited in comparison to HMF generation [21], thus, hydrolysis of carbohydrate for monosaccharide production will substantially promote LA formation. It should be noted that carbohydrate from normal lignocellulosic biomass sources is generally coated by lignin [22,23], which is more recalcitrant compared to carbohydrate

[24], making it an obstacle for efficient utilization of polysaccharides.

Here, we propose a novel, efficient, intensified one-pot cascade process for LA/ester production from cassava, an abundant and widely distributed non-edible energy crop in tropical zones such as Brazil and South China. In which, the feedstock (cassava) suffers low temperature monosaccharide formation prior to LA/ester production with efficient delignification in ethanol/H<sub>2</sub>O. Meanwhile, esterification of LA with ethanol occurs in the aqueous ethanol solution, which further enhances depolymerization of cassava. The results demonstrate that when cassava is pretreated at 100 °C for 1.0 h, 60.36% LA/ester yield with a process efficiency of 88.90% could be obtained, which are almost double that obtained without prehydrolysis.

## 2. Materials and methods

### 2.1. Materials

The cassava was kindly supplied by a local farm in Guangzhou, prior to use, it was crushed and sieved to 40–60 mesh. The starch content of this material was measured by the GB/T 5514-2008 method (the standard method utilized in China). The carbohydrate (cellulose and hemicellulose) and lignin contents were determined by the NREL method. The results show that it is composed of 75.50% starch, 12.23% cellulose, 6.41% hemicellulose and 4.58% lignin. The standard compounds of LA, HMF, furfural, formic acid and the monosaccharide were purchased from Acros (Belgium). H<sub>2</sub>SO<sub>4</sub>, NaOH, ethanol and other reagents were provided by Guangdong Guanghua Sci-Tech Co. Ltd. (Guangzhou, China). All reagents were of analytical grade and used without further purification.

### 2.2. LA and LE production

Cassava depolymerization was carried out in a 50 mL stainless steel autoclave reactor equipped with a mechanical stirring device (316L, Tongda Chemical Machinery Co. Ltd. Liaoning province, China). In typical, 3.0 g cassava, 20 mL ethanol and 10 mL 5 wt.% H<sub>2</sub>SO<sub>4</sub> aqueous were charged into the reactor in the sequence below. Air was displaced by nitrogen three times and the reactor sealed under a nitrogen atmosphere, the batch reactor was heated to 100 °C (prehydrolysis step) for 1.0 h and then heated to the designated reaction temperature (140–200 °C) for a specific time (1–5 h). When the reaction was finished, the reactor was cooled to room temperature under flowing water over 30 min. The scale-up experiment was conducted in a 1.5 m<sup>3</sup> reactor, utilizing the same procedure as the lab test.

### 2.3. Product separation and analysis

The solid was filtered and thoroughly washed using ethanol and water (v/v = 1:1) three times (10 mL × 3). Then, it was dried

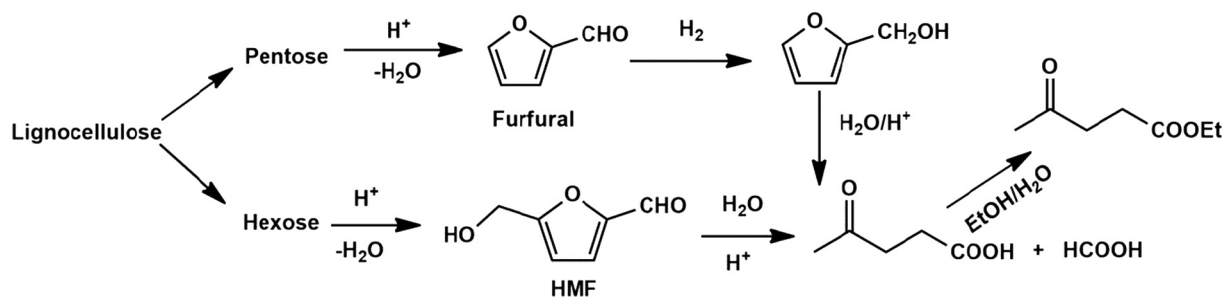


Fig. 1. Pathway for levulinic acid/ester production.

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