

Levulinic acid production integrated into a sugarcane bagasse based biorefinery using thermal-enzymatic pretreatment



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ABSTRACT

Levulinic acid (LA) is a promising platform chemical that can be produced from C6-sugars of lignocellulose. However, direct conversion of lignocellulose leads to the predefined by-products furfural and a solid residue, composed of lignin and humins. Enabling independent conversion of the major biomass components would increase the flexibility in terms of the products of a biorefinery. Therefore, this work focuses on integrating LA production into a biorefinery, which fractionates the biomass with a thermal-enzymatic treatment using hot water and enzymes only. Besides a glucose solution, used for LA production, a hemi-cellulose rich hydrolysate and solvent free lignin were recovered. The yields for the C6-fractions after thermal and enzymatic treatment were 95.8 mol% and 62.1 mol%, respectively.

The influence of temperature (160–200 °C), residence time (3–90 min) and acid concentration (0.25–1 M) on LA synthesis, following thermal-enzymatic treatment was investigated by statistical methods, achieving a maximum LA yield of 67.7 mol%.

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1. Introduction

Reduction of greenhouse gas emissions and depletion of fossil resources are among the drivers for turning our fossil-based economy into a more bio-based one. In such a bio-economy, not only fuels and energy, but also the commodities for daily needs (e.g. plastics, sanitary products, cleaning agents) should be provided from renewable resources. Although several products from renewable sources, especially from biomass, are available on global markets already, they predominantly serve niche markets. Due to the still ongoing food vs. fuel or food vs. chemicals debate, global research is focusing on using lignocellulosic residues. In particular, residues from the agricultural and forestry industry are considered as raw material (Girisuta, 2007; Rackemann et al., 2014; Morone et al., 2015; Rivas et al., 2015). To transform the vision of a bio-based economy, the production of bulk chemicals must be realized in an economically and environmentally viable way. Thus, the technolo-

gies, which are already available for a wide range of products, need to be improved.

Over the last decades, several chemicals have been identified as promising platform chemicals that can be produced from biomass, one of them being levulinic acid (LA) (Leonard, 1956; Werpy et al., 2004). With a global consumption of 2,600 t/a (2013) (Grand View Research, 2014), LA is currently serving niche markets at comparatively high prices from 5 to 8 \$/kg (2013) (Grand View Research, 2014). At present, the main consumers are the agricultural, pharmaceutical, cosmetic and food industry (Grand View Research, 2014). But due to its high functionality, given by a ketone and carboxylic group, LA can be used for a wide range of applications like polymers, plasticizers or fuel additives. Thus, a rapid growth of the market volume is expected in the near future (Leonard, 1956; Rackemann and Doherty, 2011; Grand View Research, 2014).

Levulinic acid can be synthesized, together with the co-product formic acid, from hexose through the main intermediate 5-hydroxymethylfurfural (HMF) by multiple acid catalyzed dehydration and hydrolysis reactions (Leonard, 1956; Horvat et al., 1985). Under acidic conditions repolymerization reactions of the sugars with themselves, HMF or other intermediates can form water soluble and insoluble polymers (humins) (van Dam et al., 1986).

Abbreviations: BBGS, Bagasse based glucose solution; HMF, 5-hydroxymethylfurfural; LA, Levulinic acid; LHW, Liquid hot water; MSA, Methane sulfonic acid.

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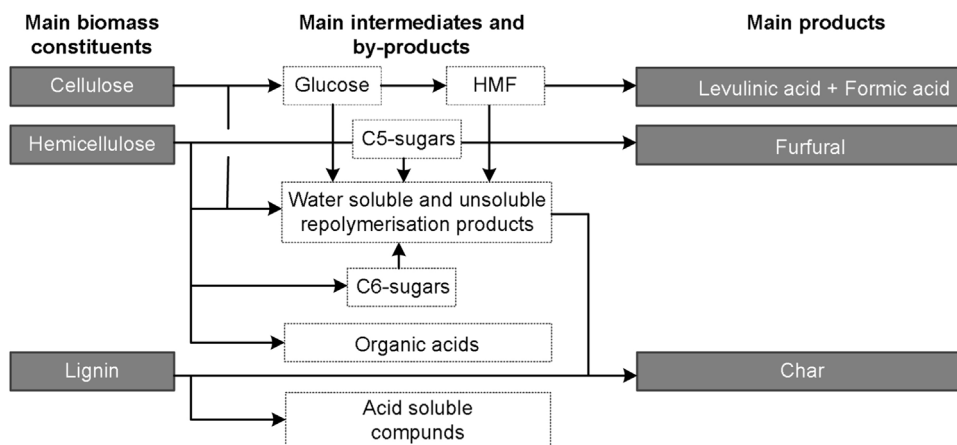


Fig. 1. Schematic conversion of the major biomass constituents during the direct conversion of lignocellulose to levulinic acid.

Although the synthesis of LA has been discussed since the 1870s, there are still multiple challenges to commercial production including catalyst selection and effective product recovery (Leonard, 1956; Morone et al., 2015). In terms of catalyst selection, dozens of possible catalysts have been investigated, whereupon the highest yields were obtained by using homogeneous catalysts, especially mineral acids like hydrochloric and sulfuric acid (Rackemann and Doherty, 2011; Morone et al., 2015).

The Biofine Process invented by Fitzpatrick (1990) was, due to high yields for LA of 70–80 mol%, for a long time the most distinguished process for LA synthesis from biomass (Raspollini-Galletti et al., 2012). In this process, lignocellulosic biomass is converted in the presence of sulfuric acid in a two reactor setup into LA, furfural and a solid residue called Biofine char. Based on this technology, Le Calorie built the first commercial-scale plant for the production of LA in Caserta, Italy which used amongst others, paper mill sludge and tobacco chops as feed material (Ritter, 2006). But at a larger scale, the technology couldn't run successfully for all feedstocks used, because depositions of humins and salts led to clogging of the reactors (Raspollini-Galletti et al., 2012). The production facility in Caserta, operated by GF biochemicals, started the production of LA in 2015 with a capacity of 2,000 t/a and plans scale up to 10,000 t/a in 2017 (Ondrey, 2015). Currently, the plant is running with starch as raw material, with the intention to switch to cellulosic feedstocks in 2016 (Ondrey, 2015). Besides a few processes running at pilot or demonstration scale, the Caserta plant is, at present, the only process running at commercial scale and the world's largest plant that produces LA directly from biomass (GF Biochemicals, 2015; Morone et al., 2015).

Fig. 1 schematically shows the acid catalyzed conversion of lignocellulosic biomass and the major products. Due to the severe process conditions for LA synthesis, the pentose sugars are not only hydrolyzed to monomeric sugars but are dehydrated to furfural or further degraded or repolymerized (Fitzpatrick, 1990).

The lignin fraction is partially converted to acid soluble compounds like vanillin or phenolic acids (Li et al., 2015; Rackemann and Doherty, 2011). The acid insoluble lignin fraction is recovered as a mixture together with the humins. Additionally, residues of the

catalyst will remain in this material, the so-called char fraction. This limits the range of application, since pure and especially sulfur-free lignins are preferred for numerous applications. Therefore, the char is currently predominantly considered for energy supply through combustion (Hayes et al., 2005). The possibility of integrating the production of LA into a biorefinery concept with prior biomass fractionation has been discussed by Rackemann and Doherty (2011) for improving the product flexibility. This concept allows the recovery of the hemicellulose sugars using a pretreatment of the biomass with milder conditions as used for LA production. The remaining biomass, which consists predominantly of cellulose and lignin, is then used for LA synthesis. Since no separation of the lignin fraction takes place; the lignin is, similar to the direct conversion, recovered together with the formed humins (Rackemann and Doherty, 2011).

In this work, the conversion of LA was analyzed in the context of a biorefinery concept, that fractionates the three major components of lignocellulosic biomass and allows independent conversions routes. The considered concept is schematically shown in Fig. 2.

Bagasse, a residue from the sugarcane industry, was used as raw material. In South Africa, around 16–20 Mio. t/a of cane are harvested (Smith et al., 2014). For every ton of cane, 130 kg of dry bagasse accrue after the sugar extraction. The bulk is used for energy provision of the mills (Gupta and Demirbas, 2010), whereas, the excess of bagasse (up to 30%) is available for further conversion (Reid and Rein, 1983). In some mills, the bagasse is already used for paper, tissue or furfural production (DalinYebo, 2012; Sappi, 2016). By optimizing the energy efficiency of the mills, the amount of excess bagasse could be even further increased (Reid and Rein, 1983).

When using bagasse, especially at larger scale, biomass supply and handling become very important, since bagasse has a very low bulk density and shows an extremely broad particle size distribution, ranging from long fibers to fine dust. This impedes efficient storage and transportation and, in terms of biomass pre-treatments, high solid loadings. Pelletizing can overcome these problems (Heinze, 2000); therefore, in this work the bagasse was pelletized prior to the investigation.

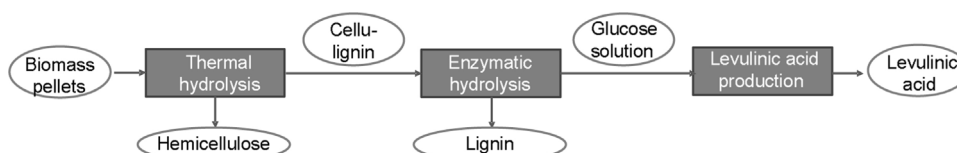


Fig. 2. Schematic flow diagram of the considered biorefinery concept for the production of LA from lignocellulosic biomass.

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