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# Optimal Flowsheet Design for Levulinic Acid Production from Lignocellulosic Biomass: a Superstructure-based Approach

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Levulinic acid is one of the twelve sugar-based building blocks selected by the US Department of Energy as the most promising biobased chemicals. The highest potential is due to the market projection of its products, such as additive for fuels (methyl tetrahydrofuran and levulinate esters), biodegradable herbicide (delta-amino acid levulinic), resins and plasticizer (diphenolic acid). The levulinic acid can be produced from lignocellulosic biomass, the most abundant and renewable feedstock, that do not compete with food production and address sustainability for biorefineries. However, this transformation is not economically feasible yet. The search for feasibility resulted in a significant number of process alternatives, which makes the flowsheet design a complex and challenging task. The present study addresses this issue by defining a superstructure that gathers some of the most promising processes described in the literature. The alternatives were modeled and combined in a mixed-integer linear programming problem that maximize the economic objective function. The optimized process flowsheet resulted in the dilute acid pretreatment of the biomass, followed by direct conversion of cellulose into levulinic acid by HCl catalysis, the solid-liquid separation of humins, flash separation of HCl, and liquid-liquid extraction and distillation of the products. This process configuration resulted in a net present value of 818 million US$, and an internal rate of return of 36%.

## 1. Introduction

Levulinic acid (LA) is a highly flexible building block that can be part of the production platform of several products and markets. Its great potential was described in the report “Top added chemicals from biomass: Volume I”, made by the US Department of Energy (DOE) (Werpy et al. 2004). LA's importance relies on the market projection based on a diverse and large volume of chemicals. Some of the main compounds available from LA are: the delta-aminolevulinic acid that is used to produce biodegradable herbicide and drugs (Rebeiz et al. 1984; Sun et al. 2018); the levulinate esters that are potential gasoline and biodiesel additives (Christensen et al. 2011; Yan et al. 2015); the diphenolic acid capable of replace the toxic bisphenol A in the polycarbonates industry (Yan et al. 2015). An interesting raw-material for LA production is the lignocellulosic biomass since it is a low-cost renewable feedstock rich in carbohydrates. The production uses the C6 carbohydrates in one-step acid-catalyzed dehydration or C5 carbohydrates that need an additional reduction step (Lopes et al., 2017). The main technical barriers are the side reactions and the development of effective heterogeneous catalysts to replace the homogeneous ones. Other barriers include expensive reactors and recovery plants, high-temperature processes resulting in high-energy consumption, high cost for catalyst recovery or waste disposal (Rackemann et al., 2011). Barriers like these depend on the technology used and directly affect the economic viability of the LA production (Silva et al., 2018). To maximize the economic return, it is important to analyze as many technologies as possible, under the same conditions so that the optimal flowsheet process can be designed.

An interesting alternative that allows the analysis of several technologies in different flowsheet options at the same time for one process is superstructure optimization. Giuliano et al. (2016) used this approach to find the optimized process flowsheet of a multiproduct biorefinery using hardwood as raw material. This study analyses different technologies to produce ethanol, succinic acid, and levulinic acid and conclude that the optimal flowsheet is dependent on the economic variables such as product selling price, discount rate, and plant scale. To the best of our knowledge, no one has used a superstructure to optimize the levulinic acid

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production from lignocellulosic biomass. This gap is addressed by gathering the most promising process on a superstructure. All units in this structure are modeled considering the mass balance and the capital and manufacturing costs. The models combined lead to an approximated mixed-integer linear programming problem that was solved by the software General Algebraic Modeling System (GAMS). The result is the definition of the optimal process flowsheet that maximizes the economic objective function. This paper first presents all the process characteristics, and then describe all the mathematic models, as well as the objective function; finally, the optimized process flowsheet is presented.

## 2. Methodology

### 2.1 Superstructure and Process Description

The biorefinery superstructure was built based on the most promising process alternatives described in the literature. It is divided into four main sections, as shown in Figure 1: pretreatment, hydrolysis, LA conversation, and downstream. Each section includes an alternative process that has the same goal.

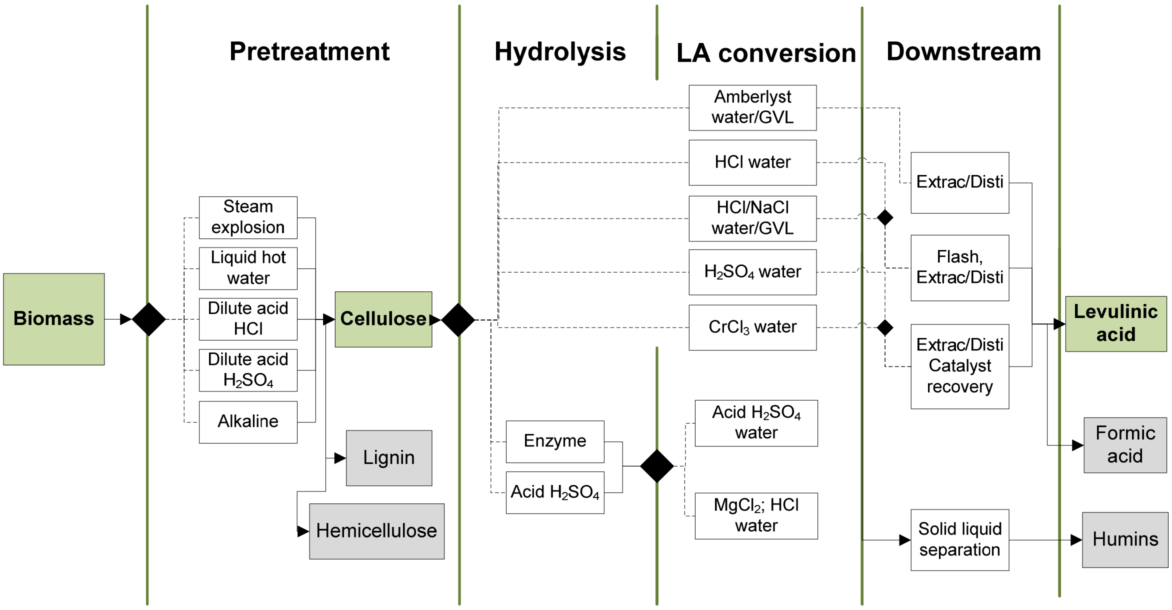

*Figure 1: Superstructure that combines the recent technologies described in the literature and considered in this study for levulinic acid production using lignocellulosic biomass as raw material.*

The pretreatment intends to fractionate the biomass into its main components (cellulose, hemicellulose, and lignin). The hydrolysis intends to hydrolyze the cellulose fraction into its monomers of glucose. The LA conversion intends to convert the cellulose directly to LA, or it converts the hydrolyzed glucose to LA. The last section is downstream that intends to purify the product streams. The section pretreatment considers five different process alternatives: steam explosion, liquid hot water, diluted acid with $H_2SO_4$, diluted acid with HCl, and alkaline pretreatment. The yield of each process alternative was obtained from experimental research done specifically with sugarcane bagasse (Table 1). The alkaline pretreatment operation was modeled as a reactor operating at 140°C, for 20 min, feed with water, and $Na_2CO_3$ as described by Nosratpour et al. (2018). Liquid hot water pretreatment was modeled as a reactor operating at 160°C for 20 min, as described by Santo et al. 2018. The steam explosion pretreatment was modeled as described by Rocha et al. (2015), operating at 190°C, 7 bars, for 15 min. The diluted acid pretreatment is the one used for ethanol production on a commercial scale, especially due to its low acid consumption. Two acid types were considered in this study, HCl and $H_2SO_4$. Both are well described in the literature, have different market prices, and present different effects on the biomass. The process was modeled as a reactor operating at 130 and 120°C, respectively. The HCl concentration was 1.25%, solid/liquid ratio of 12.5%, and residence time of 10 min, as described by Yu et al. (2013). The $H_2SO_4$ concentration was 1%, solid to liquid ratio of 1:10, and residence time of 10 min, as described by Rocha et al. (2015).

After each pretreatment, solid-liquid separation is considered. The main composition of the fractions is particular for each pretreatment. For example, the alkaline pretreatment solubilizes the lignin fraction, so the solid-liquid separation produces a lignin liquid stream and a cellulose/hemicellulose solid stream. The acid pretreatment, on the other hand, solubilizes the hemicellulose fraction. The solid-liquid separation produces a xylan/xylose liquid stream and a lignocellulose solid stream. All pretreatments considered offer a solid fraction rich in cellulose. This fraction can be directly converted to LA, or it can be hydrolyzed into glucose monomers that then will be converted in LA. The present study considers two different technologies to hydrolysate the cellulose into glucose: the acid hydrolysis and the enzymatic hydrolysis. The acid hydrolysis is catalyzed by $H_2SO_4$ that is a well-established technology on biomass hydrolysis. It was described by Kumar et al. (2015) and used a 40% (w/w) concentration of $H_2SO_4$ at 80°C, and a solid:liquid ratio of 1:4. The enzymatic hydrolysis was modeled as described by Rocha et al. (2015), and used 15 FPU $mL^{-1}$ Celluclast and 10 UI $g^{-1}$ of Novozyme in 3 g dry weight of biomass, in a citrate buffer medium.

The LA conversion depends on the depolymerization of cellulose, which is one of the main bottlenecks due to its insolubility. To overcome this issue, several technologies and catalysts were developed, each one with some pros and cons, and five of them were evaluated in this study. The mathematic model considered a conversion reactor, and the main product yield is described in Table 1. The Amberlyst technology is the only heterogeneous catalysis evaluated because, despite its advantages such as catalyst recovery, it does not generally allow good results in the experimental literature. The majority of catalysts are homogeneous such as mineral acids (HCl, $H_2SO4$) or $CrCl_3$.

*Table 1. Conversion and recovery values considered in each process alternative of the superstructure sections.*

| Section | Process/Catalyst | Conditions | | Main product Yield | Reference |
|---|---|---|---|---|---|
| | | T (°C) | p (bar) | | |
| Pretreatment | Acid $H_2SO_4$ | 120 | 1.98 | 35.5 (c) 6.5 (h) 20.8 (l) | Rocha et al., (2015) |
| | Acid HCl | 130 | 1.98 | 32.4 (c) 3.1 (h) 17.9 (l) | Yu et al., (2013) |
| | Steam explosion | 190 | 12.7 | 38.7 (c) 3.0 (h) 22.0 (l) | Rocha et al., (2015) |
| | Liquid hot water | 160 | 7 | 35.9 (c) 10.6 (h) 17.9 (l) | Santo et al., (2018) |
| | Alkaline | 110 | 1.98 | 31.2 (c) 13.8 (h) 2.8 (l) | Nosratpour et al., (2018) |
| Hydrolysis | Acid $H_2SO_4$ | 80 | | 38 | Kumar et al., (2015) |
| | Enzime | 45 | | 56 | Rocha et al., (2015) |
| LA conversion (Glucose-LA) | Acid $H_2SO_4$ | 140 | | 38 | Girisuta et al., (2006) |
| | $MgCl_2$; HCl | 140 | | 30 | Choudhary et al., (2013) |
| LA conversion (Cellulose-LA) | Amberlyst | 118 | | 49 | Alonso et al., (2013) |
| | HCl/NaCl | 155 | | 52 | Wettstein et al., (2012) |
| | HCl | 180 | | 44 | Shen et al., (2012) |
| | $H_2SO_4$ | 175 | | 43 | Girisuta et al., (2007) |
| | $CrCl_3$ | 200 | | 48 | Peng et al., (2010) |

LA purification depends on the conversion technology applied in the early stages. The eight different conversion technologies were categorized in three downstream processes that guarantee the technical suitability: (1) extraction and distillation, (2) flash, extraction and distillation (3) extraction, distillation, and catalyst recovery. All cases consider the extraction and distillation as a group of four columns needed to separate the feed mixture containing LA, formic acid, and furfural in aqueous solution. The combination of the extractor and the distillation columns have the potential to improve energy efficiency and capital cost because the fed mixture is rich in water, so removing it at the beginning of the process enables a downsized downstream. A suitable extracting solvent is furfural, a coproduct that can be recycled from the process minimizing the operating cost. This alternative was well described by Nhien, Long, and Lee, (2016), and it is suitable for the Amberlyst and $CrCl_3$ catalysis. The process composed of flash, extraction, and distillation is suitable for the LA conversion that includes HCl as the catalyst. This acid is volatile and recovered in the first step. The process composed by extraction, distillation, and catalyst recovery is suitable for the conversion that includes $H_2SO_4$ as the catalyst, as this acid is not volatile, and need a subsequent distillation column as the recovery step.

### 2.2 Mathematical modeling

The optimization problem of the superstructure consists of mass balance equations, capital, and operation cost equations and economic objective function.

Concerning the mass balance, there are equations for mixer, reactors, and separation units. The set of equations of the mixer is:

$$F_j^{out} = \sum_{s=1}^{n_s} F_j^s \qquad (1)$$

where $F_j^{out}$ and $F_j^{s}$ is the componente j mass flow rate on the outlet and inlet stream, respectively.
The set of equations of the reactors is:

$$F_p^{out} = F_r^{in} x_p + F_p^{in} \quad (2)$$

where $F_p^{out}$ and $F_p^{in}$ is the product outlet and inlet mass flow rate, respectively. $F_r^{in}$ is the reactant inlet mass flow rate and $x_p$ is the yield to product. The yield was obtained from the literature, as mentioned above.
The set of equations of the separation units is:

$$F_j^{out.i} = F_j^{in} \theta_j \quad (3)$$

where $F_j^{out}$ and $F_j^{in}$ is the outlet and inlet stream mass flow rate, respectively, and $\theta_j$ is the fractional recovery of the component j in the outlet stream i.

### 2.3 Economic Analysis and Objective Function

A cash flow analysis was made to elucidate the plant profitably of the different process configurations. The net present value (NPV) was used as the economic objective function, defined as

$$NPV = \sum_{i=0}^{25} \frac{CF_i}{(1+r)^i} \quad (4)$$

where CF is the cash flow during the operation time (r is the annual discount rate and i the correspondent year). The discounted cash flow was based on the annual cost, revenues and capital cost, as described by Giuliano et al. (2016). Some assumptions were made for the discount cash flow, such as: construction in 2 years, production length of 25 years, 350 working days per year, no subsidies on capital investment cost, no debt, 100% equity, 100% of nominal capacity in the first year, 34% tax rate, 10-year linear depreciation and no scrap value. The main market values are: levulinic acid price 5.00 US$/kg; biomass price 40 US$/t; $H_2SO_4$ cost 0.08 US$/kg; HCl cost 0.30 US$/kg. The equations mentioned combined consists of a mixed-integer linear programming problem that was solved by the software General Algebraic Modeling System (GAMS), using the solver CPLEX.

## 3. Results

To study the levulinic acid production using the lignocellulosic biomass sugarcane bagasse as raw material, some of the leading technologies described in the literature were combined in a superstructure. Based on this survey, the mathematic models of all considered processes were combined in a mixed-integer linear programming problem. The resultant problem was solved to obtain the optimized flowsheet that maximizes the net present value as an economic objective function. Figure 2 illustrates the optimized process flowsheet:

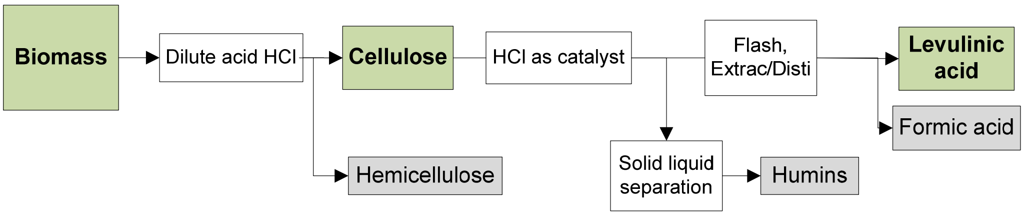

*Figure 2: Optimized process flowsheet for levulinic acid production. This process maximizes the net present value of the LA production from sugarcane bagasse as lignocellulosic raw material.*

The optimized process flowsheet includes the dilute acid pretreatment, the HCl catalysis conversion of cellulose to LA, the solid-liquid separation of humins, the downstream process composed by an HCl flash separation, followed by the LA extraction and distillation. The diluted acid pretreatment is the one used for ethanol production on a commercial scale, mainly due to its low acid consumption. Its main propose is to hydrolyze the hemicellulose fraction and facilitate the cellulose hydrolysis. The breakdown of carbohydrate fractions is an advantage because it facilitates the hemicellulose later use or sale, increasing the revenues. The same pretreatment was described by Giulliano et al. (2016) as the one that maximizes the net present value of ethanol, succinic acid, and levulinic acid production using hardwood as lignocellulosic raw material. The optimized cellulose/LA conversion technology was the one with a homogenous mineral catalyst (HCl). The proposed process was feed with 40 t/h of sugarcane bagasse and produced 6 t/h of levulinic acid. The biomass:LA ratio agrees with Khoo et al. (2016). This is an interesting technology due to its higher LA yield, modest temperatures, and low catalyst price (Gozan et al., 2017). According to Rachemann and Doherty (2011), the volatile acid catalysts provide the most uncomplicated downstream processing, allowing 90-95% recovery of the catalyst and inexpensive purification of the LA product. A flash process recovers the catalyst, which is possible because HCl is volatile and stays in the vapor stream, unlike $H_2SO_4$, TFA, and Amberlyst catalysis. This recovery step is more straightforward and less expensive than the recovery of alternative mineral acids such as sulfuric acid. The extraction before distillation is another critical factor in the economic viability of the process. Isoni et al. (2018) compared three different LA downstream alternatives using process simulation and economic investigation. According to the authors, the high water content and its heat capacity make the distillation a high-energy demand process. Therefore, the liquid-liquid extraction prior to the distillation contributes to environmental and economic suitability. The solid-liquid separation of humins is a common step in all the possible flowsheet analyzed. The humin formation can vary depending on the catalyst type, the biomass, and the process condition. It is undesirable but yet inevitable. Therefore, it is possible to suggest further studies to use this by-product to produce heat and steam that can feed the energy requirement of the plant; or study new applications for this material, as described by Mija et al. (2017). The economic analysis, as optimization result, reveled some indicators such as investment in capital cost of 154 million US$; net present value (NPV) of 818 million US$; internal rate of return (IRR) of 36%; and the payback period of 4 years. These indicators order of magnitude is according to the literature (Isoni et al., 2018). Very few studies describe the economic analysis of levulinic acid production in detail. Giuliano et al. (2016) studied levulinic acid production, among other products such as succinic acid and ethanol. In their study, the biorefinery is similar in size as the one considered in the present study (50 t/h). They found 620 million US$ NPV and 25% IRR. The smaller return can be related to the shorter plant life (20 years) and cheaper products such as ethanol (0.75%/kg versus 5.00 US$/kg of LA). Gozan et al. (2018) simulated a small LA biorefinery (40 t/day) that used *Sorghum bicolor* as raw material. They reported a 19.9% IRR and 8.6 million US$ NPV. The smaller return can be due to the small size of the biorefinery that was beneficiated by the higher LA price considered (7.62 US$/kg). The high return of investment obtained in a levulinic acid biorefinery is naturally desirable, but it is also important to address the risks associated with the implementation of such recent technologies. Differences in process conditions such as heating rates, and reactor design can influence the replicability of the yield obtained in laboratory scales on an industrial scale (Rachemann and Doherty, 2011).

## 4. Conclusions

The present study determined the optimized flowsheet process for levulinic acid production from sugarcane bagasse. The technologies that, combined, maximized the net present value of the biorefinery were: the dilute chloridric acid pretreatment of the biomass; the direct conversion of cellulose into levulinic acid by HCl catalysis; the solid-liquid separation of humins; the flash separation of HCl; the liquid-liquid extraction and distillation of the products. This process configuration resulted in a capital cost of 154 million US$, a net present value of 818 million US$, an internal rate of return of 36%, and a payback period of 4 years. Based on the results, it is possible to conclude that the levulinic acid biorefinery using sugarcane bagasse as raw material is economic suitable.

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