

# Techno-Economic Assessment of Conceptual Design for Gamma-Valerolactone Production over a Bifunctional Zr–Al–Beta Catalyst

Clara López-Aguado, Daniel Martínez del Monte, Marta Paniagua, Gabriel Morales, and Juan A. Melero\*



Cite This: *Ind. Eng. Chem. Res.* 2022, 61, 5547–5556



Read Online

ACCESS |



Metrics & More

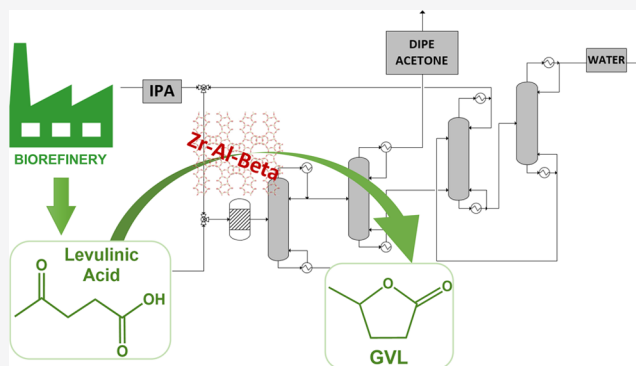


Article Recommendations



Supporting Information

**ABSTRACT:** Gamma-valerolactone (GVL) is a promising precursor for the preparation of biofuels and fuel-range hydrocarbons. This work shows the conceptual design of a process for the production of GVL from levulinic acid by means of catalytic transfer hydrogenation (CTH) over a bifunctional Zr–Al–Beta catalyst using an excess of isopropyl alcohol (IPA) acting as the hydrogen donor and solvent. The process is advantageously conducted in the liquid phase under moderate conditions, avoiding the use of high-pressure hydrogen. A techno-economic analysis of the process is presented, considering a production scale of 368.9 kg/h of GVL (ca. 85.5% GVL mass yield from levulinic acid). Such an analysis considers two main process sections, namely, (i) the reaction unit and (ii) the downstream purification section designed to achieve 99 wt % GVL purity together with 95% recovery of unreacted IPA. The analysis provides an investment of 6.4 MM€ with 7.5 MM€ annual operational costs (74% corresponding to reactants). The Minimum Selling Price for GVL is estimated to be 3076 €/ton. Finally, cost sensitivity analyses revealed the high IPA purchasing price and losses in side reactions (autoetherification) as the main obstacles to obtain a GVL competitive market price through this approach.



## 1. INTRODUCTION

The biorefinery concept implies the integrated processing of biomass resources into a range of marketable products with the concomitant production of energy. Biorefineries are expected to respond to the need for supplying a wide range of biobased products and energy in an economically, socially, and environmentally sustainable manner.<sup>1–3</sup> There is a wide variety of possibilities for a biorefinery configuration, with many processes currently in the laboratory research stage susceptible to being scaled up to real applications.

Sugar molecules coming from lignocellulosic biomass are a promising alternative to replace fossil resources. They can be further converted into intermediate chemicals, known as platform molecules, for the production of a large variety of biobased products.<sup>4–6</sup> A recognized approach to convert lignocellulose into bulk chemicals is to apply a hydrolysis treatment under moderate temperature (100–250 °C), typically using a mineral acid such as sulfuric acid, which leads to the production of levulinic acid (LA) and furfural (FAL).<sup>7–9</sup> These two platform molecules are expected to play a central role in upcoming emerging industries for the production of biobased commodities.<sup>10</sup>

In this context, LA conversion to gamma-valerolactone (GVL) is an encouraging application. GVL exhibits attractive physicochemical properties, such as biodegradability and low toxicity as well as excellent fuel characteristics. Moreover, GVL

can be used as a precursor for the production of advanced biofuels and polymers.<sup>11–15</sup> The transformation of LA to GVL occurs in a cascade reaction including hydrogenation and dehydration steps.<sup>10,16,17</sup> On the one hand, this reaction system is well-studied in the literature and has been successfully catalyzed by different heterogeneous catalysts.<sup>18–24</sup> On the other hand, with the purpose of avoiding the use of gas H<sub>2</sub> and high-pressure reaction facilities, the reduction step can be accomplished by means of a liquid-phase catalytic transfer of hydrogen (CTH) through the Meerwein-Ponndorf-Verley (MPV) mechanism using a sacrificial alcohol as a hydrogen donor.<sup>25,26</sup> During the last years, our group has thoroughly studied the one-pot transformation of biomass-derived precursors into GVL, integrating the catalysis of acid-driven and hydrogen-transfer (MPV) steps over a unique bifunctional Al–Zr–Beta catalyst. This catalyst has been shown to efficiently promote the direct transformation of LA into GVL using isopropyl alcohol (IPA) as a hydrogen

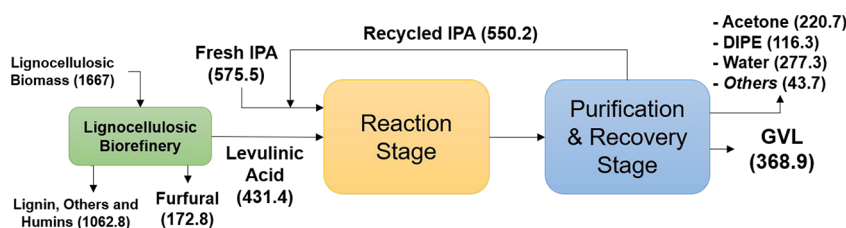
**Received:** December 1, 2021

**Revised:** April 2, 2022

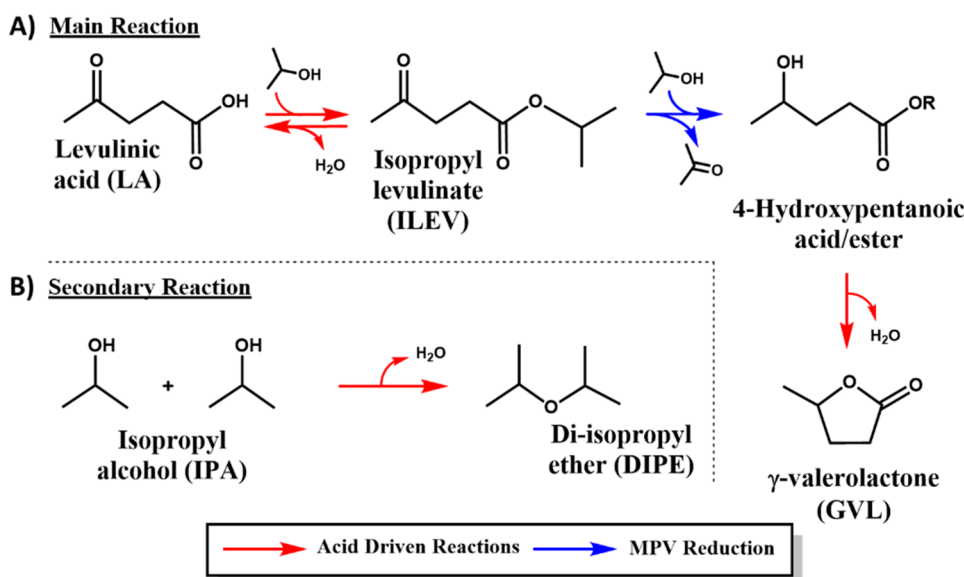
**Accepted:** April 5, 2022

**Published:** April 18, 2022





**Figure 1.** Conceptual scheme and mass balances (kg/h) of the proposed process for the large-scale production of GVL from biorefinery-derived LA using IPA as hydrogen donor and solvent. *Others* in the outlet of the Purification & Recovery Stage indicate other remaining chemicals in a small quantity (ILEV, LA, GVL, and IPA).



**Figure 2.** Chemical transformations experimentally observed in the production of GVL from LA in IPA. (A) Cascade reaction for the transformation of LA into GVL in the presence of Zr–Al–Beta catalyst; (B) acid-catalyzed autoetherification of IPA.

donor.<sup>27,28</sup> The use of such one-pot systems would allow for avoiding the necessity of intermediate separation and purification downstream stages, potentially reducing the energy needs and capital costs.

LA production is already a well-known process described in the scientific and patent literature. In fact, some demonstration plants are already working using hydrolytic technologies to produce LA or levulinate esters, like those proposed in Biofine or Dibanet processes.<sup>29,30</sup> In contrast, GVL production from lignocellulosic LA has been only studied on a bench scale.<sup>5</sup> At lab scale, we optimized the one-pot production of GVL from LA over Zr–Al–Beta catalyst, reaching high GVL yield and selectivity.<sup>27,28</sup> In a step forward in the transition of this process from research to industrial stage, herein we provide a techno-economic analysis to elucidate its feasibility as well as to identify the potential bottlenecks and process areas to be improved.

The techno-economic analysis herein presented involves five steps: (i) process definition and reaction kinetics analysis to settle the simulation; (ii) simulation of the proposed conceptual process using *Aspen Plus* software; (iii) equipment sizing and cost analysis to obtain the total capital investment (TCI), the total annualized costs (TAC), and the GVL minimum selling price (MSP); (iv) sensitivity analyses to determine the influence of feedstock price (LA and IPA) and the extent of the undesired side reactions; and (v) heat integration to enhance the energy efficiency of the overall process.

## 2. APPLIED METHODOLOGY

The methodology proposed in the present study comprises five steps: (1) process definition; (2) modeling and simulation of the integrated process; (3) economic analysis; (4) sensitivity analysis; and (5) energy analysis. Each step is described in detail below.

**2.1. Step 1: Process Definition.** Figure 1 summarizes the concept and overall mass balance of an industrial plant operating with LA as feedstock to produce GVL in a single reaction stage using a bifunctional Zr–Al–Beta catalyst and considers the integration within a biorefinery complex.<sup>29,30</sup> The designed process also includes a train for GVL purification and IPA excess recovery. In the reaction stage, LA is transformed into GVL in a single catalytic step in the presence of IPA as solvent and hydrogen donor (technical data for this reaction step are derived from our previous results on bench-scale experiments).<sup>27</sup> The reaction block comprises a stirred batch reactor and the necessary auxiliary equipment, such as mixer, pump, and heater for the feedstock conditioning and product stream management. The reaction stage is followed by a purification and recovery stage to reach GVL commercialization specifications (99 wt % purity) and maximize the recovery of unreacted IPA for recycling. On the basis of our experimental data, a high excess of IPA is necessary to maximize the yield to GVL. In this way, more than 50% of IPA fed to the reactor remains unconverted, the recovery of which is essential to make the process economically competitive.

Considering the compounds present in the products stream, and their differences in boiling point, distillation appears as the most appropriate unit operation to apply. Thus, this second block of the process includes several distillation columns and auxiliary equipment (pumps, condensers, etc.). Detailed information regarding the design of the main equipment is provided in section 3. The integrated process shows an overall lignocellulose-to-GVL yield of 22 wt % and LA-to-GVL yield of 85.5 wt %.

For the kinetic analysis, the reaction pathway shown in Figure 2 was followed. Experimental data allowed settling the kinetic parameters necessary to perform the simulation of the reaction stage in the *Aspen Plus* software. Selected reaction conditions are based on our previous experimental optimization studies performed at a bench scale.<sup>27</sup> Thus, lab-scale experiments were performed in a stainless steel stirred autoclave (200 mL) fitted with a temperature controller and a pressure transducer under autogenous pressure. The reaction conditions were: temperature, 170 °C, concentration of levulinic acid (LA, Sigma-Aldrich, 98%), 2 mol·L<sup>-1</sup>, isopropyl alcohol (IPA, Scharlau, 98%), 80 mL, and catalyst loading, 37.5 g·L<sup>-1</sup>. To avoid mass transfer limitations, the stirring rate was fixed at 1000 rpm, and the reaction mixture was heated to the desired temperature (~30 min heating time). Reaction aliquots were periodically withdrawn, up to 24 h, and filtered to remove catalyst particles before analysis. Reaction products were analyzed using a Varian 3900 gas chromatograph equipped with an Agilent CP-WAX 52 CB column (30 m × 0.25 mm, film thickness (DF) = 0.25 μm) and a flame ionization detector (FID). Isopropyl levulinate (ILEV) was detected as the only intermediate product of the cascade reaction (no 4-hydroxypentanoic acid was detected, indicating its fast transformation into GVL). Since it is not a commercially available product, it was synthesized by the esterification of LA with IPA using sulfuric acid as catalyst reaching 98% purity in order to calibrate gas chromatography (GC) and allow its quantification.<sup>31</sup>

Catalytic results were monitored in terms of absolute conversion of LA ( $X_{LA}$ ) and yields toward the different products ( $Y_i$ ). Likewise, GVL concentration ([GVL]) was calculated to perform the kinetics adjustment. In addition, the formation of di-isopropyl ether (DIPE) was detected and quantified using GC. DIPE comes from the IPA autoetherification side reaction, which is unavoidably catalyzed under the selected reaction conditions by the Brønsted acid sites present in the Al–Zr–Beta catalyst. The definitions of these reaction parameters are as follows (eqs 1–4).

$$X_{LA} = \frac{\text{reacted mol of LA}}{\text{initial mol of LA}} \times 100 \quad (1)$$

$$Y_i = \frac{\text{formed mol of } i}{\text{initial mol of LA}} \times 100 \quad (2)$$

$$[\text{GVL}] (\text{mol}\cdot\text{L}^{-1}) = [\text{LA}]_0 \times Y_{\text{GVL}} \quad (3)$$

$$Y_{\text{DIPE}} = \frac{2 \cdot \text{formed mol of DIPE}}{\text{initial mol of IPA}} \times 100 \quad (4)$$

**2.2. Step 2: Modeling and Simulation of the Integrated Process.** The purpose of this step is to simulate the process proposed in the definition step to meet the required product specification. Process modeling and simulation were performed using *Aspen Plus* software v.11 (Aspen

Tech). Figure S1 (Supporting Information) shows the process simulation diagram. The *Non-Random Two-Liquids* (NRTL) model was selected for the estimation of thermodynamic properties, considering the deviation from ideality of the mixtures under study. The reaction system for the conversion of LA to GVL was modeled as a *Continuous Stirred-Tank Reactor* (CSTR) applying the kinetic parameters obtained from the experimental results. Heat exchangers, modeled as HeatX, and pumps were included for the conditioning of process streams to the required levels of temperature and pressure, respectively.

In the separation and purification section (Figure 1), all the distillation columns were simulated using the RADFRAC rigorous model. The number of distillation stages and molar reflux ratios were optimized for each column following the method of minimum Distillation Annualized Costs (DAC) (eq 5).

$$\text{DAC} = \frac{\text{capital cost}}{\text{payback period}} + \text{utility costs} \quad (5)$$

Utility costs are associated with the energy requirements to condense or evaporate the streams from the distillation columns, whereas capital costs are related to the infrastructure and materials integrating the columns. According to the literature, a payback period of three years has been assumed for calculations. In order to optimize the feed plate, a sensitivity analysis was performed on each column, the optimum feed plate being the one minimizing the reboiler duty.<sup>32</sup>

Mass and energy balances from the simulation (included as Table S1 in the Supporting Information) were used to obtain the size of the main pieces of equipment (reactor, distillation columns, exchangers, and pumps). The resulting design parameters are included in Table S2.

**2.3. Step 3: Economic Analysis.** An economic analysis was performed on the overall process based on data generated in the previous process simulation. Total Capital Investment (TCI), Total Annualized Costs (TAC), and the Minimum Selling Price of GVL (MSP<sub>GVL</sub>) (€/ton of GVL) were estimated using the mass and energy balances as well as the equipment design parameters (Tables S1 and S2, respectively).

The inside battery limits (ISBL) capital investment for GVL processing was estimated using the factorial method (see details in Table S3). The outside battery limits (OSBL) investment is assumed to be 40% of the ISBL, while engineering charges and contingencies are taken as 25% and 10% of the combined (ISBL + OSBL) costs, respectively. Equipment costs were calculated using bibliographic methods and heuristic correlations.<sup>33</sup> The resultant costs were updated using the annualized Industrial Price Index (IPRI) to the current year, as provided by the Spanish National Institute of Statistics<sup>34</sup> (see details in the Supporting Information). Hence, the TCI includes the Inside and Outside Battery Limits (ISBL, OSBL), the Design and Engineering costs (D&E), and a Contingencies item (C). Likewise, the costs assigned to the initial catalyst and reactant loadings into the reactor have also been considered within the Total Capital Investment.

Finally, amortization costs were estimated for a 10-year period ( $n$ ) with an interest rate ( $i$ ) of 20% according to eq 6.

$$\text{amortization costs } (\text{€}) = \frac{\text{TCI} \cdot i}{1 - \left(\frac{1}{1+i}\right)^n} \quad (6)$$

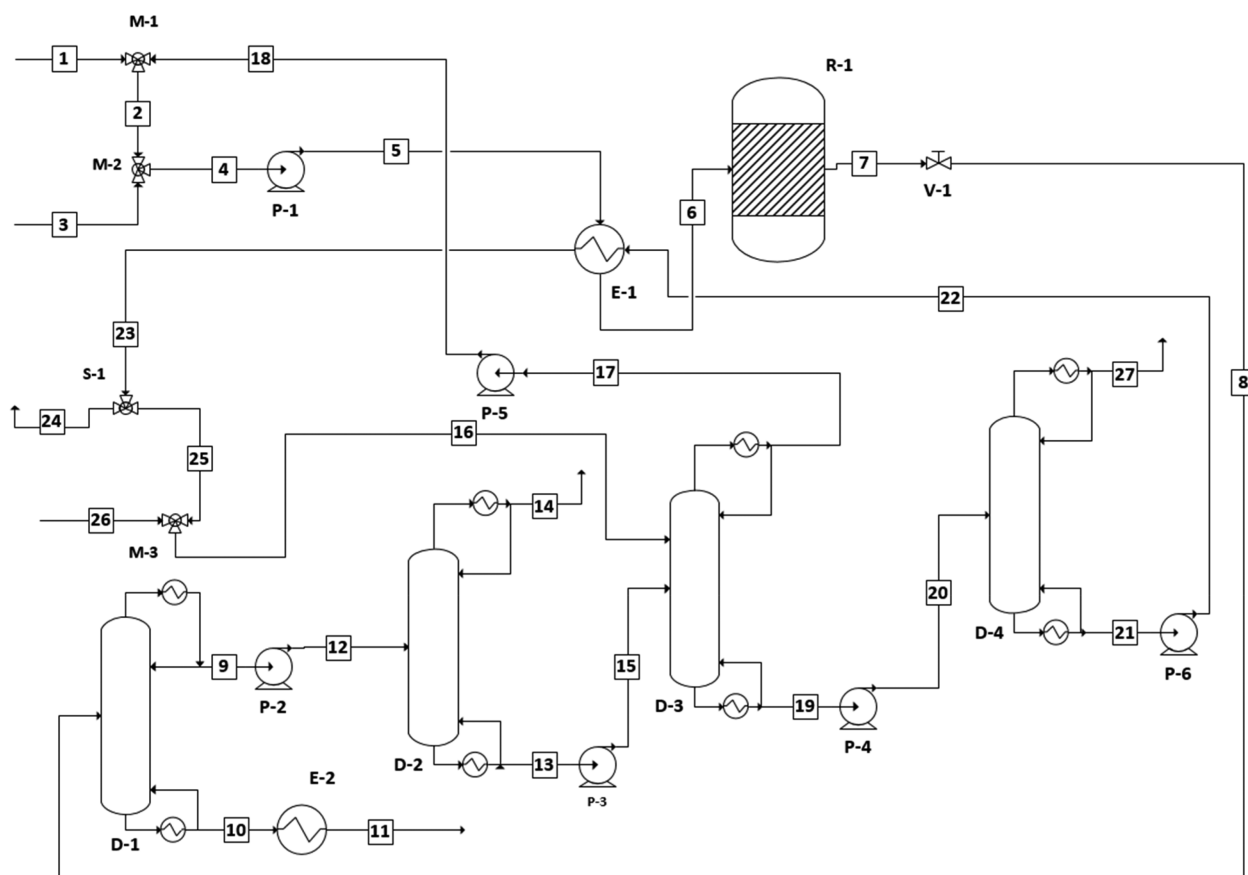


Figure 3. Flow diagram of the conceptual design of the GVL production process from LA via CTH with IPA over Zr–Al–Beta catalyst.

However, the TAC were estimated considering the feedstock and utilities consumptions (unitary prices of feedstock and utilities, as well as consumption of utilities, are available in Tables S4 and S5, respectively). Other economic parameters required to calculate the operational costs and to complete the economic analysis (e.g., maintenance, salaries, insurances, royalties, and licenses) are available in Table S6.<sup>35,36</sup> Finally, combining the calculated TAC, the amortization costs, and the annual production of GVL, the MSP of GVL can be determined (eq 7). Noteworthy, the GVL annual production was estimated considering 8000 operating hours per year and the result of the simulation mass balance (Table S1).

$$\text{MSP (€ / ton)} = \frac{\text{amortization costs (€ / y)} + \text{TAC (€ / y)}}{\text{GVL production (ton / y)}} \quad (7)$$

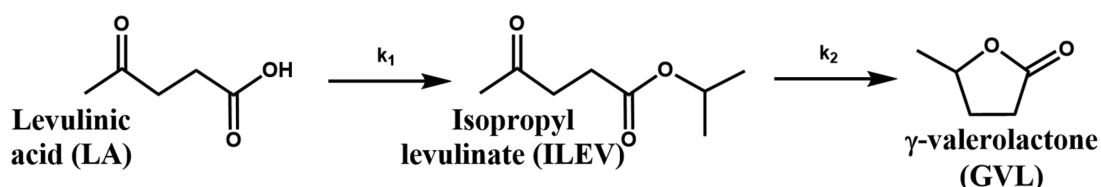
**2.4. Step 4: Sensitivity Analysis.** The developed economic model allows one to perform sensitivity analyses to show the potential of the proposed process as well as to elucidate the influence of selected operation variables on the  $\text{MSP}_{\text{GVL}}$ . Thus, the impact of LA and IPA selling prices (€/kg) was analyzed by varying them in the range of  $\pm 20\%$ . Likewise, since the extent of the side reaction of DIPE formation has shown a strong influence on the amount of fresh IPA fed to the reactor, the yield to DIPE was also chosen for the sensitivity analysis. We note that modifying the yield to DIPE implies the use of different reaction conditions and/or catalyst, so the results of this analysis would present a higher degree of uncertainty. Considering this, the DIPE yield was varied in the range of  $\pm 36\%$ , the lower value meaning a negligible extent of

this undesired reaction. For both variables, the worst and best potential scenarios were recalculated.

**2.5. Step 5: Energy Analysis.** The energy analysis was performed using the *Aspen Energy Analyzer* module, included in the *Aspen Plus* software. To calculate the energy-saving potential and to optimize the heat-exchangers network, the composite curve (Figure S2) was built from the thermal data provided by the simulation. The composite curve allows one to estimate the minimum hot and cold utilities requirements by overlapping the heat source and heat sink profiles, considering between them a minimum temperature difference of  $10\text{ }^{\circ}\text{C}$  (pinch point). Thus, an additional energy scenario based on a different configuration for the heat-exchangers network was applied to study the influence of the energy optimization in terms of utilities savings, which in turn would have a beneficial impact on the GVL minimum selling price.

### 3. PROCESS DESIGN AND FLOW DIAGRAM

Raw LA is obtained by a chemical hydrolysis of lignocellulosic biomass, for example, through a Biofine or Dibanet process.<sup>29</sup> For a definition of the scale of the techno-economic analysis, the mass flow rate of  $1667\text{ kg/h}$  of lignocellulosic biomass was selected with the following composition (dry basis): 50 wt % cellulose, 20 wt % hemicellulose, 20 wt % lignin, and 5 wt % ashes (the rest being water-soluble compounds and a lipid fraction). This biomass flow rate corresponds to a demonstration plant processing 40 tons of dry lignocellulose per day.<sup>29,30</sup> The acid hydrolysis of the (hemi)cellulosic fraction of the biomass yields the following products: furfural (FAL), levulinic acid (LA), and formic acid as well as degradation



**Figure 4.** Proposed simplified reaction scheme for the kinetic analysis of the LA transformation into GVL in the presence of IPA and Zr–Al–Beta catalyst.

products (humins) and other minor compounds. Hence, considering a theoretical maximum efficiency for the C6-sugar fraction transformation of 70% (as demonstrated by the Biofine or Dibanet processes), the inlet LA mass flow rate for the simulation and economic analysis was fixed at 431.4 kg/h.

Figure 3 shows the flow diagram of the designed GVL production process, starting from LA and using IPA as hydrogen donor over a Zr–Al–Beta catalyst. The overall process can be divided into two stages, namely, (i) the reaction section and (ii) GVL purification and IPA recovery.

**3.1. Reactants Conditioning and Reaction Stage.** LA and IPA streams are mixed (M-2), pressurized to 26 bar (P-1), and heated to 170 °C using a heat exchanger (E-1) that uses the heat from the solvent recirculation stream (glycerol) avoiding the use of additional heat exchangers (Figure 3). The preheated feed stream is then fed to the CSTR reactor, wherein the main and secondary reactions take place simultaneously in the reaction media (see Figure 2). On the one hand, the cascade transformation of LA into GVL, involving (i) the esterification of LA with IPA to produce the respective levulinate (ILEV), (ii) the catalytic transfer hydrogenation, whereby the carbonyl moiety in the formed ILEV is reduced to the corresponding alcohol, yielding the highly reactive intermediate isopropyl 4-hydroxy pentanoate, and finally (iii) a fast lactonization to yield the GVL target product. In this transformation GVL is the main reaction product with some remaining traces of ILEV as well as acetone and water as byproducts. Additionally, on the one hand, nonreacted IPA remains in the output stream. On the other hand, IPA can condense by autoetherification forming diisopropyl ether (DIPE). As it will be shown, this undesired side reaction has a high impact on the economic feasibility of the process.

According to this reaction scheme, the modeling of the reaction stage was performed using two virtual parallel blocks: (i) a first reactor modeled as a CSTR block, where the conversion and product selectivity are obtained by means of a calculator block using the experimental kinetic data, and (ii) a second reactor modeled as a *Stoichiometric Reactor* (RStoic), based on the experimental yield of DIPE recorded under the bench-scale optimized reaction conditions (36% mol). Both reaction blocks in the simulation scheme take place simultaneously within the same global reaction stage.

To obtain the kinetic parameters for the direct transformation of LA to GVL over Al–Zr–Beta catalyst, we proposed the simplified reaction scheme depicted in Figure 4. The proposed kinetic model includes a first catalytic step for the esterification of LA to ILEV ( $k_1$ ), followed by a second catalytic step involving both the MVP reduction of ILEV and the subsequent fast lactonization of 4-hydroxy pentanoate into GVL ( $k_2$ ). As experimentally observed, mass balances from quantified species were close to 100%, so that the formation of

degradation byproducts, for example, humins, was considered negligible.

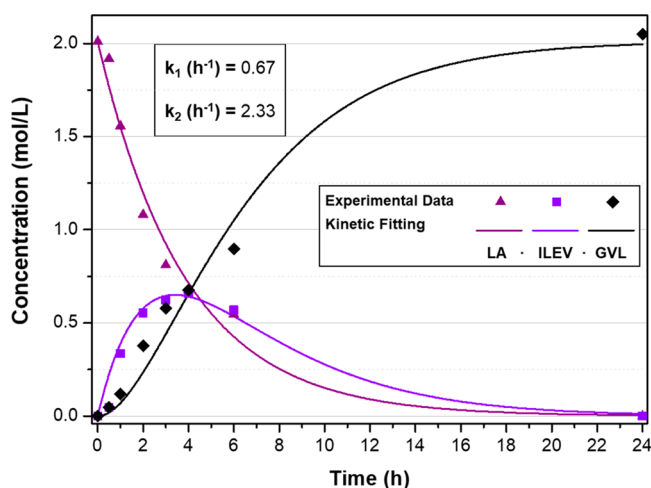
According to the cascade reaction shown in Figure 4, a pseudohomogeneous kinetic model was proposed (eqs 8–10).

$$\frac{dC_{LA}}{dt} = -k_1 C_{LA} \quad (8)$$

$$\frac{dC_{ILEV}}{dt} = k_1 C_{LA} - k_2 C_{ILEV} \quad (9)$$

$$\frac{dC_{GVL}}{dt} = k_2 C_{ILEV} \quad (10)$$

Here,  $C$  is the molar concentration of each component, and  $k_i$  is the apparent first-order kinetic constant of step  $i$  at a constant temperature. The fitting of experimental data to the kinetic model is depicted in Figure 5, showing a high accuracy of the model. The values of the calculated apparent kinetic constants are also included in Figure 5.



**Figure 5.** Experimental (symbols) and simulated (lines) data obtained from the kinetic model corresponding to the cascade transformation of LA into GVL over Al–Zr–Beta catalyst. Reaction conditions: temperature 170 °C; LA/catalyst: 0.083 mol·g<sup>-1</sup>; IPA: 80 mL.

As shown, the ILEV transformation into GVL is the fastest step ( $k_2 = 2.33 \text{ h}^{-1}$ ), so the concentration of ILEV goes through a maximum and rapidly decreases. Aiming at a complete LA conversion as well as to the maximum yield to GVL, a reaction time of 24 h was chosen for the design of the reactor in the simulated process.

**3.2. GVL Purification and IPA Recovery.** Separation and purification steps are required to attain high-purity GVL (99 wt %) and to recover the unreacted IPA for recycling. Since all compounds involved in the process can be condensed at atmospheric pressure, all distillation columns are assumed to

operate at 1 bar. Table S7 shows the design specifications as well as the calculation results corresponding to the necessary distillation train.

The reactor outlet stream (stream 7, Figure 3) has a mass flow rate of 1565.5 kg/h, GVL and IPA being the main components (23.6 and 36.9 wt %, respectively). However, there are also significant amounts of acetone, water, and, especially, DIPE. GVL can be almost completely recovered from the bottom of distillation column D-1 (Figure 3). The column design was performed specifying 99 wt % GVL purity and 99% GVL recovery as bottoms. The distillate stream (stream 9) contains a mixture of acetone, DIPE, IPA, water, and traces of GVL. The obtained GVL stream is then cooled to 40 °C (E-2) and driven to the storage section (stream 11). Stream 9 is separated into a mixture of IPA and water (bottom, stream 13) and acetone and DIPE (top, stream 14) in a second distillation column D-2. The design specification for column D-2 is to achieve a bottom stream containing an acetone mass composition below 1 wt %.

Next in the purification section, IPA must be recovered from the IPA and water mixture for alcohol recycling to the reaction stage. Unfortunately, IPA forms an azeotrope with water at atmospheric pressure, not allowing one to perform a purification via conventional distillation.<sup>37</sup> Thus, IPA separation and recovery was performed by means of extractive distillation in column D-3 using a solvent as entrainer.<sup>38</sup> After different alternatives were analyzed, glycerol was chosen as the extracting solvent because it enhances the relative volatility of IPA over water. Moreover, glycerol shows a relatively low cost and high availability due to its condition as a byproduct in the biodiesel industry.<sup>39</sup> The distillate stream of column D-3 (stream 17) contains a mass composition of ca. 96 wt % of IPA, which is recycled to the reactor. Finally, glycerol is completely recovered in distillation column D-4 (stream 21) and used for the preheating of the inlet stream to the reactor (stream 5) before being recycled back to the extractive column D-3.

For the sake of simplicity, the purification of the DIPE coming from the autoetherification of IPA was not considered in the proposed purification and recovery section. However, this compound has the potential to be used as solvent as well as oxygenated gasoline additive. In consequence, it has a market price that would ideally help to improve the economy of the present process. Therefore, a further proposal for future studies should also consider including a DIPE purification section.

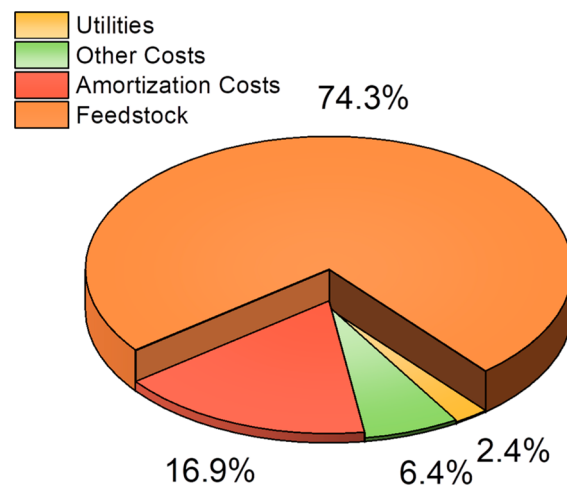
## 4. RESULTS AND DISCUSSION

**4.1. Economic Analysis: Production and Costs.** This section shows the results corresponding to the Total Capital Investment, the Total Annualized Costs, and the GVL Minimum Selling Price estimated for the analyzed process. The proposed biorefinery approach considers an industrial capacity of 40 tons of dry lignocellulose per day, which in turn results in the production of 431.4 kg/h of LA. With this input, a mass flow of 368.9 kg/h of produced GVL is achieved. Considering a standard working capacity of 8000 operating hours per year, the proposed plant would have an annual production of 2952 GVL tons. Table 1 summarizes the results of the techno-economic analysis as well as the main parties required for the estimation of the  $MSP_{GVL}$  (see details in the *Techno-economic analysis* Section in the [Supporting Information](#)).

**Table 1. Total Capital Investment (TCI), Total Annualized Costs (TAC), and Minimum Selling Price (MSP) of GVL for the Simulated Process of LA Transformation into GVL**

Total Capital Investment [TCI] (€)	6 441 303
Inside Battery Limits [ISBL]	3 364 401
Outside Battery Limits [OSBL]	1 345 760
Design & Engineering [D&E]	1 177 540
Contingencies [C]	471 016
Feedstock & catalyst (initial loading)	82 585
Amortization Costs (€/year)	1 536 397
Total Annualized Costs [TAC] (€/year)	7 541 178
Feedstock (€/year)	6 745 371
Levulinic acid	1 432 331
Isopropyl alcohol	5 294 955
Catalyst	8883
Glycerol	9202
Utilities (€/year)	216 089
High-pressure steam	107 498
Medium pressure steam	62 148
Cooling water	44 245
Electricity	2199
Others (€/year)	579 177
GVL production (ton/year)	2952
$MSP_{GVL}$ (€/ton)	3076

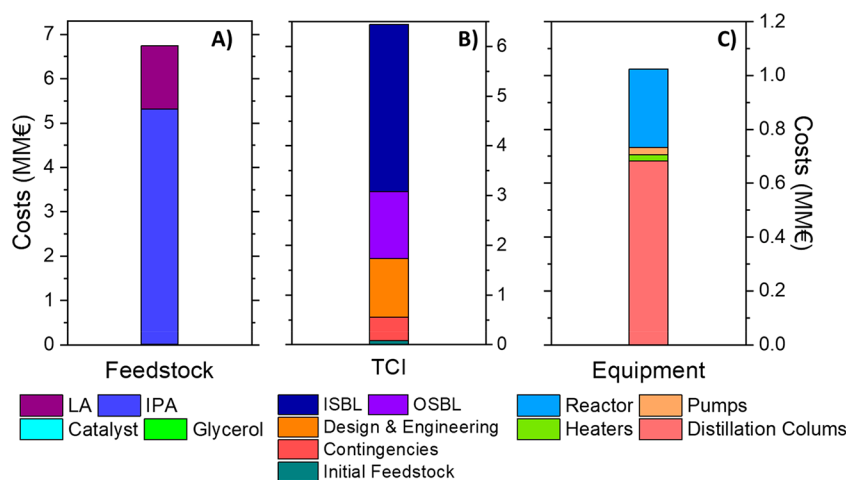
Table 1 shows a breakdown of the annual operating costs to produce GVL estimated at 7.5 MMC. The TAC includes all the operating costs for GVL production, such as feedstock, utilities, and other costs. Since there are no previous studies related to the proposed process, and considering that the catalyst employed has been demonstrated to be stable for over 450 h in a continuous flow reactor,<sup>28</sup> the catalyst life has been assumed as three years, which is also a typical catalyst time replacement for fuel production processes.<sup>40</sup> Figure 6 shows



**Figure 6.** Costs distribution for the estimation of the  $MSP_{GVL}$  (%).

the contribution of the different items of the TAC in the  $MSP_{GVL}$ . The cost of feedstock is clearly the main contributor (ca. 74%), with a very small contribution from the utilities (<3%).

Figure 7A compares the feedstock costs for each reagent. LA can display an optimized purchasing price of 500 \$/ton,<sup>29,30</sup> whereas IPA, which is a solvent with many industrial applications and with great demand in different sectors, was



**Figure 7.** Costs distribution (MM€) for the simulated process of LA transformation into GVL. (A) Feedstock supply, (B) TCI, and (C) required equipment.

listed in 2018 with an average purchasing price of 1150 €/ton.<sup>41</sup> Thus, the relatively high market prices of LA and IPA, together with the need of feeding a large flow rate of fresh solvent due to losses in the undesired side reaction, make both reactants represent close to 100% of the total feedstock cost. In contrast, the almost complete recovery of glycerol in the process, as well as the high stability of the catalyst, render them as negligible items in terms of production costs.

The TCI required is estimated in 6.4 MM€. Figure 7B shows the contribution of the different items in the overall TCI. The ISBL investment is ca. 3.4 MM€, which considers the installed equipment and associated components acting upon the primary feed stream processing (equipment purchases and settlement, piping, electric systems, etc.). Thereafter comes the OSBL with 1.3 MM€, which is related to equipment pieces and associated components supporting the whole ISBL, and finally, the Design & Engineering of the process, with 1.2 MM€. A concept of Contingencies is required to cover possible unexpected expenses (0.5 MM€). Finally, the initial feedstock, required to switch on the production until a steady-state level, closes the TCI cost. In this proposal, TCI is paid off for 10 years and with an interest rate of 20%, which implies 1.5 MM€ of annual amortization costs.

The installed equipment considered in the ISBL concept comprises the elements necessary for GVL production and purification as well as for IPA recovery and recycling. As shown in Figure 7C, the distillation columns and the reactor (made of stainless steel) are the most expensive equipment in the plant (ca. 95% of the total equipment cost). The separation train is composed of four distillation columns, adding to a total cost of 682 k€ (67% of the total equipment cost). On the one hand, the complex separation of the azeotropic IPA–water mixture significantly raises the equipment needs involved in the separation strategy. On the other hand, the reactor cost is 28% of the total equipment (292 k€), due to the high mass flow rate fed into it and the long residence time (fixed at 24 h from the experimental kinetic analysis, Figure 5). Finally, the cost of heaters and pumps for streams conditioning only supposes 5% of the total equipment cost (51 k€).

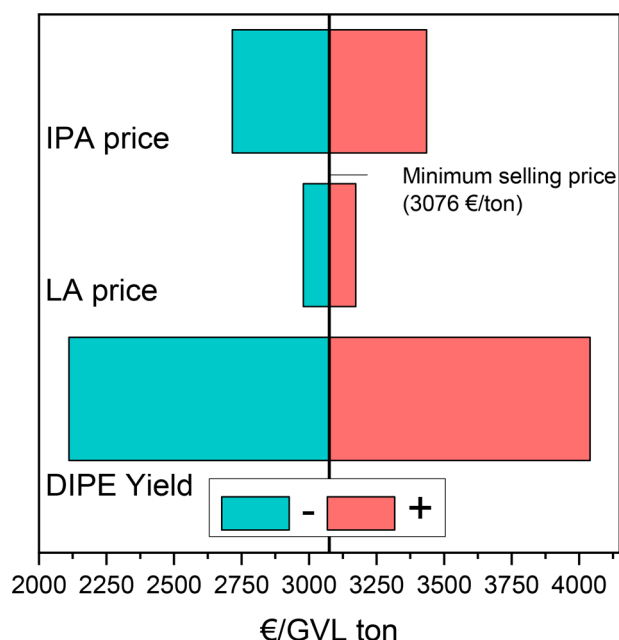
MSP<sub>GVL</sub> is also included in Table 1. The high mass yield in the production of GVL starting from LA, the simplicity of the reaction process, and the low requirements of auxiliary services, result in a moderate MSP<sub>GVL</sub> of 3076 €/ton. This value is in

the range of other works reported in literature for the production of GVL using different strategies (1.25–3.88 \$/ton).<sup>42</sup> Unfortunately, the high purchasing costs of the raw materials (LA and IPA) make the process not economically competitive with current equivalent oil-derived commodities. However, considering other added benefits of the present strategy, like the sustainability and green origin of GVL coming from renewable lignocellulosic biomass, together with the increasing implementation of restrictions to the use of fossil fuels, it can be foreseen that the current approach will gain competitiveness in the future.

**4.2. Sensitivity Analysis.** Sensitivity analyses were conducted to identify the relative significance of key process parameters affecting the MSP<sub>GVL</sub>. The selected parameters were, on the one hand, IPA and LA purchasing prices (€/ton), and, on the other hand, the DIPE molar yield (%). DIPE formation implies the collateral undesired consumption of IPA, thus having a strong influence on the final product selling price. As previously described, the sensitivity analyses were performed applying a  $\pm 20\%$  variation in the prices of reactants and a  $\pm 36\%$  variation in the DIPE yield. For each case, the MSP<sub>GVL</sub> was recalculated and compared to the base scenario (Figure 8).

As shown, the most significant parameter under study is the IPA purchasing price, either directly or in the form of IPA consumption to produce DIPE (undesired side reaction). So, it is identified as the parameter having the highest impact on the annualized costs. As we mentioned earlier, the technical grade price for the base economic analysis was fixed at 1150 €/ton IPA, as reported by ICIS.<sup>41</sup> However, this value is subjected to market fluctuations and might vary insofar as the product demand oscillates. When considering an IPA market price drop of 20%, the GVL selling price decreases to 2716 €/ton (−11.7%). On the contrary, in the scenario where IPA price increases 20%, the GVL selling price increases to 3413 €/ton (+11.7%). Such variations are directly proportional to TAC, strongly affecting the final MSP<sub>GVL</sub> and the overall profitability of the proposed process.

However, the LA purchasing price seems to be less significant, at least in the range of market prices herein considered. Its expected market price for large-scale production is estimated at 500 \$/ton,<sup>29</sup> but this value is likely to be reduced when new and more efficient biorefinery



**Figure 8.** Sensitivity analyses on  $MSP_{GVL}$  studying a 20% fluctuation of IPA and LA price and a 36% fluctuation of DIPE molar yield.

technologies reach market application, aside from the positive effect of process scaling-up in large industries. Thus, for a  $\pm 20\%$  fluctuation in the LA price, the  $MSP_{GVL}$  varies only by a modest figure of  $\pm 3.2\%$  (from 2978 to 3173 €/ton, respectively).

Finally, the DIPE yield was also studied because of its strong influence on the final  $MSP_{GVL}$ : the higher the DIPE yield, the more amount of fresh IPA must be fed into the system to maintain the IPA/LA mass ratio. Under the used experimental conditions, the DIPE yield is 36 mol %, so almost 576 kg/h of fresh IPA must be fed into the process to compensate the loss in the form of DIPE. In a best-case ideal scenario, where the experimental conditions and/or the catalyst acidity would not promote DIPE formation, it would only be necessary to replace the IPA consumed in the MPV reduction ( $\sim 266$  kg/h). Under such hypothetical conditions, and assuming that the production of GVL remains unaltered despite the modification of reaction conditions and/or catalyst, the  $MSP_{GVL}$  would decrease to 2111 €/ton ( $-31.3\%$ ). On the contrary, when the DIPE yield grows 36%, the  $MSP_{GVL}$  rises sharply to 4040 €/ton ( $+31.3\%$ ). These figures highlight the importance of further research in the design of advanced bifunctional catalysts for reducing the side reaction of DIPE formation.

**4.3. Energy Analysis.** Through the *Aspen Energy Analyzer* and the composite curve obtained (Figure S2), an additional alternative scenario was set by increasing in three units the heat exchanger network. Figure S3 shows the flow diagram of this alternative GVL production process from LA, including the new heat exchangers recommended by the *Energy Analyzer* module to save energy. The heat exchanger E-A1 integrates the enthalpies of the upstream to condenser D-4 and the upstream to reboiler D-2. On the one hand, since the upstream to exchanger E-2 is at a high temperature, it is possible to take advantage of its temperature to preheat the bottom stream of column D-2. On the other hand, it is necessary to use cooling water to keep the temperature of the reactor R-1. Thus, the R-1 downstream heated water can be used to preheat the upstream to reboiler D-4.

The base-case scenario requires an energy input value of 1099 kW. This value comprises the high-pressure and the medium-pressure steam usage in the process. An increase in the number of units and the subsequent increase of the exchange area to 3.22 m<sup>2</sup> leads to a decrease in the energy input down to 983 kW in the alternative-case scenario. On the contrary, it is possible to observe a similar decrease in the energy required to produce 1 kg of GVL from 111.5 to 99.7 MJ/ton GVL, as the heat exchanger areas increase by adding additional units or shells. However, since the energy optimization herein proposed does not reflect a significant effect on the GVL production cost (IPA price keeps being the key parameter affecting the  $MSP_{GVL}$ ). Moreover, as a potential additional improvement from the energy point of view, the process heat demand might be advantageously compensated by the combustion of the biomass solid residues discarded in the biorefinery.

## 5. CONCLUSIONS

A conceptual design of the process for the production of GVL from LA over a Zr–Al–Beta bifunctional catalyst has been developed, based on experimental data obtained at the bench scale. A complete process simulation has been performed using the software *Aspen Plus*. Reaction and separation sections have been thoroughly analyzed, aiming at reaching high GVL purity and recovery of unreacted IPA. As a result, the necessary design variables have been defined and calculated, allowing the performance of a complete techno-economic analysis. On the one hand, such a techno-economic analysis applied to the proposed process has identified the high amount of IPA required for the process (consumed in both the production of GVL and the side reaction of DIPE formation), as well as the high purchasing price thereof, as the main variables affecting the  $MSP_{GVL}$ . On the other hand, the production cost for LA has a much lower influence (in the range of values herein considered for large-scale production). Thus, an  $MSP_{GVL}$  of 3076 €/kg has been obtained, in the upper range of values reported in the literature for this chemical. Sensitivity analyses have shown that a  $\pm 20\%$  fluctuation in the feedstock purchasing price has a proportional effect on the  $MSP_{GVL}$ , being much more significant for the more expensive IPA. In the foreseeable scenario where the purchasing price of raw materials will decrease substantially (due to technology evolution and a large-scale economy) and the side reaction of IPA autoetherification is advantageously minimized by selecting more appropriate catalysts and/or reaction conditions, the  $MSP_{GVL}$  for this GVL production approach will become competitive and attractive in the market.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c04644>.

*Aspen Plus* process simulation flowsheet for the production of GVL from LA via CTH using IPA as hydrogen donor; mass balance of the production of GVL from LA; techno-economic analysis: correlations for the estimation of equipment costs; calculated design parameters and equipment costs; calculation of the TCI using the factorial method; utilities and feedstock costs used for the estimation of TAC; stated variables of the thermal utilities used in the process; other annual



costs used in the techno-economic evaluation; design specifications and calculated data for distillation columns; composite curve (obtained using ASPEN Energy Analyzer); flow diagram of the process using an energy integration strategy (PDF)

### Special Issue Paper

Originally intended for the special issue Prof. José Luis García Fierro Festschrift, *Ind. Eng. Chem. Res.* 2021, Volume 60, Issue 51.

## AUTHOR INFORMATION

### Corresponding Author

Juan A. Melero – Chemical and Environmental Engineering Group, Universidad Rey Juan Carlos, E-28933 Madrid, Spain; [orcid.org/0000-0002-7591-2720](https://orcid.org/0000-0002-7591-2720); Email: [juan.melero@urjc.es](mailto:juan.melero@urjc.es)

### Authors

Clara López-Aguado – Chemical and Environmental Engineering Group, Universidad Rey Juan Carlos, E-28933 Madrid, Spain; [orcid.org/0000-0002-1511-6861](https://orcid.org/0000-0002-1511-6861)

Daniel Martínez del Monte – Chemical and Environmental Engineering Group, Universidad Rey Juan Carlos, E-28933 Madrid, Spain

Marta Paniagua – Chemical and Environmental Engineering Group, Universidad Rey Juan Carlos, E-28933 Madrid, Spain; [orcid.org/0000-0002-2485-5121](https://orcid.org/0000-0002-2485-5121)

Gabriel Morales – Chemical and Environmental Engineering Group, Universidad Rey Juan Carlos, E-28933 Madrid, Spain; [orcid.org/0000-0002-5070-4749](https://orcid.org/0000-0002-5070-4749)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.iecr.1c04644>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research has been funded by Spanish Ministry of Science, Innovation and Universities, Grant No. RTI2018-094918-B-C42, and Regional Government of Madrid, Grant No. S2018/EMT-4344 (CM-BIOTRES).

## ABBREVIATIONS

CTH = catalytic transfer hydrogenation  
DAC = distillation annualized costs  
DIPE = di-isopropyl ether  
FAL = furfural  
GC = gas chromatography  
GVL =  $\gamma$ -gamma-valerolactone  
ILEV = isopropyl levulinate  
IPA = isopropyl alcohol  
IPRI = Industrial Price Index  
ISBL = Inside Battery Limits  
LA = levulinic acid  
MPV = Meerwein-Ponndorf-Verley reduction  
MSP = minimum selling price  
NRTL = Non-Random Two-Liquids  
OSBL = Outside Battery Limits  
RCSTR = Continuous Stirred-Tank Reactor  
RStoic = Stoichiometric Reactor  
TAC = total annualized costs  
TCI = total capital investment

## REFERENCES

- (1) Vlysidis, A.; Binns, M.; Webb, C.; Theodoropoulos, C. A Techno-Economic Analysis of Biodiesel Biorefineries: Assessment of Integrated Designs for the Co-Production of Fuels and Chemicals. *Energy* **2011**, *36* (8), 4671–4683.
- (2) de Jong, E.; Jungmeier, G. Biorefinery Concepts in Comparison to Petrochemical Refineries. In *Industrial Biorefineries & White Biotechnology*; Elsevier, 2015; pp 3–33. DOI: 10.1016/B978-0-444-63453-5.00001-X.
- (3) Nizami, A. S.; Rehan, M.; Waqas, M.; Naqvi, M.; Ouda, O. K. M.; Shahzad, K.; Miandad, R.; Khan, M. Z.; Syamsiro, M.; Ismail, I. M. I.; Pant, D. Waste Biorefineries: Enabling Circular Economies in Developing Countries. *Bioresour. Technol.* **2017**, *241*, 1101–1117.
- (4) Bozell, J. J.; Petersen, G. R. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the US Department of Energy’s “Top 10” Revisited. *Green Chem.* **2010**, *12* (4), 539.
- (5) Isikgor, F. H.; Becer, C. R. Lignocellulosic Biomass: A Sustainable Platform for the Production of Bio-Based Chemicals and Polymers. *Polym. Chem.* **2015**, *6* (25), 4497.
- (6) Alonso, D. M.; Hakim, S. H.; Zhou, S.; Won, W.; Hosseinaei, O.; Tao, J.; Garcia-Negron, V.; Motagamwala, A. H.; Mellmer, M. A.; Huang, K.; Houtman, C. J.; Labbé, N.; Harper, D. P.; Maravelias, C.; Runge, T.; Dumesic, J. A. Increasing the Revenue from Lignocellulosic Biomass: Maximizing Feedstock Utilization. *Sci. Adv.* **2017**, *3* (5), No. e1603301.
- (7) Chang, C.; Cen, P.; Ma, X. Levulinic Acid Production from Wheat Straw. *Bioresour. Technol.* **2007**, *98* (7), 1448–1453.
- (8) Mukherjee, A.; Dumont, M. J.; Raghavan, V. Review: Sustainable Production of Hydroxymethylfurfural and Levulinic Acid: Challenges and Opportunities. *Biomass and Bioenergy* **2015**, *72*, 143–183.
- (9) Fang, Z.; Smith, R. L.; Xinhua Qi, J. *Production of Platform Chemicals from Sustainable Resources*; Fang, Z., Smith, R. L., Qi, X., Eds.; Biofuels and Biorefineries; Springer Singapore: Singapore, 2017. DOI: 10.1007/978-981-10-4172-3.
- (10) Pileidis, F. D.; Titirici, M. M. Levulinic Acid Biorefineries: New Challenges for Efficient Utilization of Biomass. *ChemSusChem* **2016**, *9* (6), 562–582.
- (11) Horváth, I. T.; Mehdi, H.; Fábos, V.; Boda, L.; Mika, L. T.  $\gamma$ -Valerolactone—a Sustainable Liquid for Energy and Carbon-Based Chemicals. *Green Chem.* **2008**, *10* (2), 238–242.
- (12) Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. Integrated Catalytic Conversion of  $\gamma$ -Valerolactone to Liquid Alkenes for Transportation Fuels. *Science* (80-). **2010**, *327* (5969), 1110–1114.
- (13) Yao, K.; Tang, C. Controlled Polymerization of Next-Generation Renewable Monomers and Beyond. *Macromolecules* **2013**, *46* (5), 1689–1712.
- (14) Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. Gamma-Valerolactone, a Sustainable Platform Molecule Derived from Lignocellulosic Biomass. *Green Chem.* **2013**, *15* (3), 584.
- (15) Osatiashtiani, A.; Lee, A. F.; Wilson, K. Recent Advances in the Production of  $\gamma$ -Valerolactone from Biomass-Derived Feedstocks via Heterogeneous Catalytic Transfer Hydrogenation. *J. Chem. Technol. Biotechnol.* **2017**, *92* (6), 1125–1135.
- (16) Gong, Y.; Lin, L.; Yan, Z. Catalytic Hydrogenation and Oxidation of Biomass-Derived Levulinic Acid. *BioResources* **2011**, *6* (1), 686–699.
- (17) Wright, W. R. H.; Palkovits, R. Development of Heterogeneous Catalysts for the Conversion of Levulinic Acid to  $\gamma$ -Valerolactone. *ChemSusChem* **2012**, *5* (9), 1657–1667.
- (18) Du, X.-L.; Bi, Q.-Y.; Liu, Y.-M.; Cao, Y.; Fan, K.-N. Conversion of Biomass-Derived Levulinic Acid and Formate Esters into  $\gamma$ -Valerolactone over Supported Gold Catalysts. *ChemSusChem* **2011**, *4* (12), 1838–1843.
- (19) Galletti, A. M. R.; Antonetti, C.; De Luise, V.; Martinelli, M. A Sustainable Process for the Production of  $\gamma$ -Valerolactone by Hydrogenation of Biomass-Derived Levulinic Acid. *Green Chem.* **2012**, *14* (3), 688–694.

- (20) Hengne, A. M.; Rode, C. V. Cu-ZrO<sub>2</sub> Nanocomposite Catalyst for Selective Hydrogenation of Levulinic Acid and Its Ester to  $\gamma$ -Valerolactone. *Green Chem.* **2012**, *14* (4), 1064–1072.
- (21) Luo, W.; Deka, U.; Beale, A. M.; Van Eck, E. R. H.; Buijinninx, P. C. A.; Weckhuysen, B. M. Ruthenium-Catalyzed Hydrogenation of Levulinic Acid: Influence of the Support and Solvent on Catalyst Selectivity and Stability. *J. Catal.* **2013**, *301*, 175–186.
- (22) Yang, Y.; Gao, G.; Zhang, X.; Li, F. Facile Fabrication of Composition-Tuned Ru-Ni Bimetallics in Ordered Mesoporous Carbon for Levulinic Acid Hydrogenation. *ACS Catal.* **2014**, *4* (5), 1419–1425.
- (23) Tan, J.; Cui, J.; Cui, X.; Deng, T.; Li, X.; Zhu, Y.; Li, Y. Graphene-Modified Ru Nanocatalyst for Low-Temperature Hydrogenation of Carbonyl Groups. *ACS Catal.* **2015**, *5* (12), 7379–7384.
- (24) Kasar, G. B.; Medhekar, R. S.; Bhosale, P. N.; Rode, C. V. Kinetics of Hydrogenation of Aqueous Levulinic Acid over Bimetallic Ru-Ni/MMT Catalyst. *Ind. Eng. Chem. Res.* **2019**, *58* (43), 19803–19817.
- (25) Hengne, A. M.; Malawadkar, A. V.; Biradar, N. S.; Rode, C. V. Surface Synergism of an Ag-Ni/ZrO<sub>2</sub> Nanocomposite for the Catalytic Transfer Hydrogenation of Bio-Derived Platform Molecules. *RSC Adv.* **2014**, *4* (19), 9730–9736.
- (26) Gilkey, M. J.; Xu, B. Heterogeneous Catalytic Transfer Hydrogenation as an Effective Pathway in Biomass Upgrading. *ACS Catal.* **2016**, *6* (3), 1420–1436.
- (27) Morales, G.; Melero, J. A.; Iglesias, J.; Paniagua, M.; López-Aguado, C. From Levulinic Acid Biorefineries to  $\gamma$ -Valerolactone (GVL) Using a Bi-Functional Zr-Al-Beta Catalyst. *React. Chem. Eng.* **2019**, *4* (10), 1834–1843.
- (28) López-Aguado, C.; Paniagua, M.; Melero, J. A.; Iglesias, J.; Juárez, P.; López Granados, M.; Morales, G. Stable Continuous Production of  $\gamma$ -Valerolactone from Biomass-Derived Levulinic Acid over Zr-Al-Beta Zeolite Catalyst. *Catalysts* **2020**, *10* (6), 678.
- (29) Hayes, D. J.; Ross, J.; Hayes, M. H. B.; Fitzpatrick, S. The Biofine Process: Production of Levulinic Acid, Furfural and Formic Acid from Lignocellulosic Feedstocks. In *Biorefineries-Industrial Processes and Products*; Wiley, **2005**; Vol. 1, p 139.
- (30) DIABNET. DIBANET Final Publishable Summary Report; DIABNET; DIABNET, 2013.
- (31) Geboers, J.; Wang, X.; De Carvalho, A. B.; Rinaldi, R. Densification of Biorefinery Schemes by H-Transfer with Raney Ni and 2-Propanol: A Case Study of a Potential Avenue for Valorization of Alkyl Levulinates to Alkyl  $\gamma$ -Hydroxypentanoates and  $\gamma$ -Valerolactone. *J. Mol. Catal. A Chem.* **2014**, *388–389*, 106–115.
- (32) Luyben, W. L. *Front Matter*; John Wiley & Sons, Ltd, 2006. DOI: 10.1002/9781118510193.fmatter.
- (33) Towler, G.; Sinnott, R. Economic Evaluation of Projects. In *Chemical Engineering Design*; Elsevier: Boston, MA, 2013; pp 389–429. DOI: 10.1016/B978-0-08-096659-5.00009-2.
- (34) Instituto Nacional de Estadística <https://www.ine.es/>.
- (35) Towler, G.; Sinnott, R. Estimating Revenues and Production Costs. In *Chemical Engineering Design*; Elsevier: Boston, MA, 2013; pp 355–387. DOI: 10.1016/B978-0-08-096659-5.00008-0.
- (36) Cruz, P. L.; Iribarren, D.; Dufour, J. Life Cycle Costing and Eco-Efficiency Assessment of Fuel Production by Coprocessing Biomass in Crude Oil Refineries. *Energies* **2019**, *12* (24), 4664.
- (37) Boli, E.; Dimou, E.; Voutsas, E. Separation of the Isopropanol-Water Azeotropic Mixture Using Ionic Liquids. *Fluid Phase Equilib.* **2018**, *456*, 77–83.
- (38) Niu, M. W.; Rangaiah, G. P. Retrofitting an Isopropanol Process Based on Reactive Distillation and Propylene-Propane Separation. *Chem. Eng. Process. Process Intensif.* **2016**, *108*, 164–173.
- (39) Navarrete-Contreras, S.; Sánchez-Ibarra, M.; Barroso-Muñoz, F. O.; Hernández, S.; Castro-Montoya, A. J. Use of Glycerol as Entrainer in the Dehydration of Bioethanol Using Extractive Batch Distillation: Simulation and Experimental Studies. *Chem. Eng. Process. Process Intensif.* **2014**, *77*, 38–41.
- (40) Paterson, W. R. *Petroleum Refining: Technology and Economics*, 3rd ed.; 1995; Vol. 56. DOI: 10.1016/0923-0467(95)80014-x.
- (41) Palagacheva, Y. Europe IPA spot prices fall on propylene. Independent Commodity Intelligence Services (ICIS), 2018.
- (42) Kim, J.; Han, J. Simulation Study of a Strategy to Produce Gamma-Valerolactone from Ethyl Levulinate. *Energy* **2018**, *163*, 986–991.

## Recommended by ACS

### Techno-Economic Assessment and Sensitivity Analysis of Glycerol Valorization to Biofuel Additives via Esterification

Krutarth Pandit, Haresh G. Manyar, *et al.*

MAY 31, 2023  
INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

READ 

### Kinetic Analysis of Glycerol Esterification Using Tin Exchanged Tungstophosphoric Acid on K-10

John Keogh, Haresh Manyar, *et al.*

OCTOBER 26, 2022  
INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

READ 

### Hydrogen-Bond-Promoted Sucrose Conversion in a Separable Eutectic Mixture Solvent System

Mingfu Li, Jian Zhang, *et al.*

JULY 07, 2022  
ACS SUSTAINABLE CHEMISTRY & ENGINEERING

READ 

### Sustainable Upgrade of Bioderived Glycerol to Solketal through Acetalization over Metal-Free Mordenite Catalysts

Bhavna Saini, Nagabhatla Viswanadham, *et al.*

JANUARY 12, 2022  
ACS SUSTAINABLE CHEMISTRY & ENGINEERING

READ 

Get More Suggestions >