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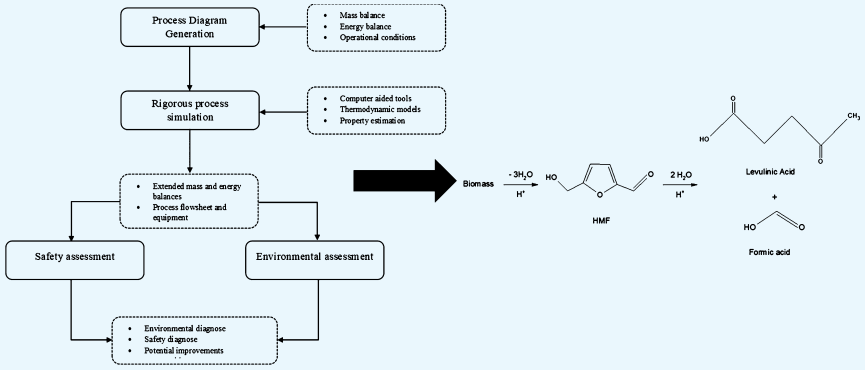
Environmental and Safety Assessments of Industrial Production of Levulinic Acid via Acid-Catalyzed Dehydration

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Supporting Information



ABSTRACT: These days, there is a need to develop novel and emerging processing pathways that permit production of value-added substances and fuels considering sustainability aspects. In this sense, levulinic acid (LA) is one of the most promising biorefinery products. This paper presents environmental and safety assessments of LA production via acid-catalyzed dehydration (ACD) of biomass. The process was modeled by using Aspen Plus process simulation software based on a capacity of 132 000 tons per annum of banana rachis (main raw material). Likewise, environmental and safety assessments were developed. Parameters such as heats of reaction, explosivity, toxicity of substances, and operational conditions along with extended mass and energy balances were used to perform safety and environmental analyses. In this regard, the modeled topology showed an inherent safety index (ISI) score of 24 with an equal contribution of 12 points for both chemical inherent safety index (CIS) and process inherent safety index (PIS). ACD showed a good safety performance, with moderate concerns related to the handling of formic acid. Moreover, the waste reduction algorithm (WAR) was used to assess environmental performance and estimate potential environmental impacts (PEIs) of the simulated topology. It was performed considering four case studies to determine the influence of mass streams (case 1), product streams (case 2), energy streams (case 3), and simultaneous products and energy contribution (case 4). This analysis showed that for this process, the total inletting flow of impacts that enter was less than the amount of these that leave the system according to a generation rate of the PEI for case 1 (-1.89×10^2 PEI/h) and case 3 (-1.83×10^2 PEI/h). From the environmental viewpoint, the major concern is associated with the photochemical oxidation potential category because of the handling of volatile organic compounds through the process.

INTRODUCTION

The environmental implications related to the use of fossil energy sources generate one of the major concerns of modern scientific society. During the last 50 years of 20th century, it is estimated that CO_2 emissions substantially increased. This fact has impacted in such a way that the Earth has suffered the effects of climate change, holes in the ozone layer, and acid rain, among others.[1] In Colombia, it is well-known that some effects associated with the climatic change has generated problems of shortages and increased in the family basket prices. It has affected the agroindustry production over this country.[2] Therefore, the development of sustainable chemical processes and cleaner production are emerging as a crucial concept for generating design alternatives in order to decrease the dependence of fossil fuels and also to promote better use of the natural resources.[3] Levulinic acid (LA) is a promising product in biorefinery processing. This substance is obtained through rehydration of 5-hydroxymethyl-furfural (HMF) which is a key component in the acid-catalyzed dehydration (ACD) process. Also, formic acid is formed as a coproduct of this reaction. HMF is extracted/produced from lignocellulosic biomass through prehydrolysis/hydrolysis stage.[4] LA has

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attracted a lot of interest because of its high market value and as an important intermediate for generation of substances for application in fuel additives, solvents, and plasticizers, among others.[5]

Environmental assessment allows evaluating suitable processing routes for chemical, physical, or biochemical processes. There are many studies describing the role of environmental assessment of promising/emerging processing technologies as a decision-making tool. Patel et al.[6] performed a life cycle assessment (LCA) of algal hydrothermal liquefaction to assess environmental impacts for biocrude production for a variety of scenarios, reporting that the modeled cultivation and hydrothermal liquefaction technology represented about 90% of the total environmental charges emitted by this process. DeRose et al.[7] assessed the production of renewable fuels from low lipid algae with the aim of selecting the processing route with the best economic and environmental performance. Meramo-Hurtado et al.[8] developed a computer-aided environmental assessment of a biorefinery for hydrogen production via a biomass gasification process. This research presented the evaluation of different purification stages for product extraction. Moreno-Sader et al.[9] used environmental analysis (along with exergy analysis) for selecting bio-oil feedstock and processing pathways through computer-aided tools. Otherwise, environmental assessment was applied to assess processing alternatives for ethylene production compared to biochemical and fossil-based pathways.[10] Hernández et al.[11] assessed an olive stone biorefinery based on technoeconomic and environmental assessment. Both analyses allowed screening the best design for this case study.

Another important aspect that should be taken into consideration in process design is the evaluation of industrial safety. A variety of methods and indicators are proposed in the literature to evaluate safety performance of chemical processes. Heikkila[12] mentioned that the Dow Fire and Explosion Index (Dow F&EI) is one of the most widely used methods in chemical industry processes, although indicators such as the prototype index of inherent safety and the inherent safety index (ISI) are also implemented. Kidam et al.[13] discussed different approaches for the evaluation of inherent safety by index methods. Moreover, several studies have addressed process evaluation of existing and emerging technologies based on safety assessment. Thiruvenkataswamy et al.[14] developed a safety and technoeconomic analysis of ethylene production technologies. Rathnayaka et al.[15] presented a methodology for decision-making in the design and analysis of chemical processes considering safety parameters. The proposed metric incorporated a novel parameter for quantifying the reduction of consequences and probability of accident occurrence through inherent safety optimization. Quddus et al.[16] developed a risk assessment of class 3 for hazardous materials in transportation. Otherwise, Song et al.[17] presented a novel framework and method for assessing inherent process safety into a conceptual design of chemical processes. As described, environmental and safety analyses are relevant methodologies and metrics widely applied to evaluate and screen suitable chemical processes considering sustainability. Thus, this study presents an environmental and safety assessment, by using the Waste Reduction Algorithm (WAR) and the ISI of synthesis of LA from lignocellulosic biomass via ACD. Technical data required to perform such process analyses were provided by modeling of the proposed topology.

RESULTS AND DISCUSSION

The chemical composition of banana rachis assumed in this study is summarized in Table 1. This raw material is classified as lignocellulosic biomass, so the lignin and hemicellulose contents of these substances are slightly higher compared to those of other biomass sources. This chemical composition was taken from the data reported by Igbinadolor and Onilude.[18] Due to its chemical structure and concentration of constituent substances, pretreatment and prehydrolysis stages are required to increase sugar production yields. Therefore, such sugar extraction methods become into crucial stages in order to obtain required concentration of pentoses (C5) and hexoses (C6), and these units should be extremely efficient.

Table 1. Chemical Composition of Banana Rachis

component	concentration (wt %)
cellulose	42.0
hemicellulose	13.0
lignin	12.0
ash	4.7
acetate	10.0
moisture	19.0

Simulation of LA Production via ACD. The process flowsheet diagram of the ACD pathway for LA production is given in Figure 1. Operational parameters such as pressure, temperature, mass fractions, and main process flows are summarized in Table 2. This proposed process is comprised of three main units: acid pretreatment (PT), acid dehydration reaction (AC), and distillation (DT). PT-1 represents the feed flow of banana rachis (main raw material), at this stage, feedstock is assumed to be already washed and milled. It is sent to a tank for mixing with H_2SO_4. This solid−liquid mixture is preheated by a heat exchange unit for reaching optimal temperature conditions before entering the pretreatment reactor. In this stage, 7% of glucan (cellulose) is hydrolyzed to form glucose, while 90% of hemicellulose is converted into xylose. Likewise, 5% of lignin is further solubilized. The other C5 carbohydrates (arabinan, mannan, and galactan) present in the biomass structure are assumed to be hydrolyzed under the same conditions as hemicellulose.[19] The process uses a flash separation unit, where huge amounts of water and impurities are removed from the main stream. Because of the presence of H_2SO_4, the flow is sent to ion-exchange and over-liming units in order to decrease the pH of the mixture. Following this, solids and liquids are separated by a hydrocyclone process; this stage divides the flow between cellulose (PT-23) and xylose (PT-24). Solubilized xylose and cellulose are separated to avoid inhibitory effects and decrease in the conversion rates of glucose formation in an enzymic hydrolysis unit.[20] The cellulose flow is sent to a hydrolysis unit for hexose production, while the pentose stream is sent to an ion-exchange unit followed by an over-liming stage for removal of impurities. Finally, extracted pentoses are directly sent to the acid-catalyzed reactor unit.

In the AC unit, the cellulose stream is used for C6 production via a hydrolysis reaction. This stage is performed through cellulase enzyme. The biological reactor operates at 30 °C and 1 atm pressure. Cellulase enzyme is assumed to be a group of coenzymes, which are composed of endoglucanases for polymer size reduction, exoglucanases for chemical hydrolysis, and b-glucosidase for cellobiose hydrolysis to produce glucose.[21] The

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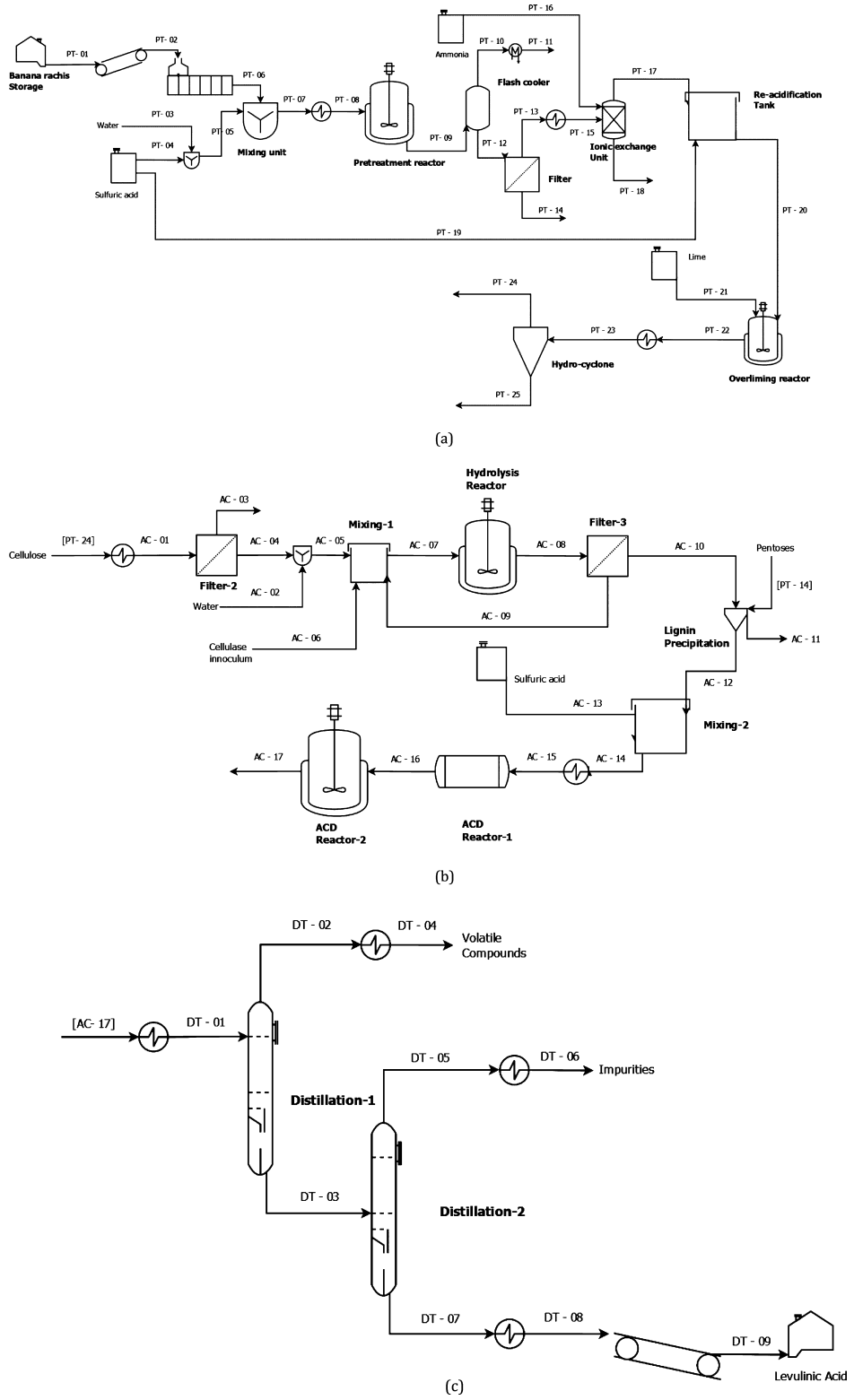


Figure 1. Process simulation flowsheet of a modeled pathway for LA production. (a) Acid pretreatment unit. (b) Acid dehydration reaction unit. (c) Distillation unit.

main chemical reaction of enzyme hydrolysis and the mass fraction yield to product (FYP) are shown in eq 1.

$$(\text{Cellulose})_n + n\text{H}_2\text{O} \rightarrow n\text{glucose} \qquad \text{FYP: } 0.90 \qquad (1)$$

Both glucose and pentose flows are delignified before the ACD reaction, which is developed to avoid inhibitory reactions, and it is commonly accomplished by using a precipitator agent. These streams are mixed and subsequently sent to a dehydration reactor for LA production. The acid-catalyzed system is comprised of two reactor stages. In the first one, glucose is converted into HMF in a plug-flow reactor which operates at 210 °C and 24.67 atm. The main stream, containing the

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Table 2. Operational Parameters and Mass Flows of Main Streams in the ACD Process

mass flow (TPA)	146 540	204 288	97 114	90 123	90 123	38 371
temperature (°C)	28.00	190.00	29.71	180.00	90.00	28.00
pressure (atm)	1.01	13.17	1.01	1.01	1.01	1.01
component\streams	PT-01	PT-09	AC-09	AC-15	DT-01	DT-09
mass concentration (kg/kg)						
H_2O	0.19	0.40	0.17	0.24	0.34	0.00
lignin	0.12	0.09	0.17	0.00	8.60×10^{-5}	2.02×10^{-4}
cellulose	0.42	0.28	5.88×10^{-2}	0.00	0.00	0.00
hemicellulose	0.13	5.00×10^{-3}	1.02×10^{-2}	0.00	0.00	0.00
ash	0.05	3.30×10^{-2}	3.10×10^{-4}	6.73×10^{-4}	6.73×10^{-4}	1.58×10^{-3}
xylose	0.00	9.40×10^{-2}	8.76×10^{-4}	9.71×10^{-2}	2.42×10^{-4}	5.69×10^{-4}
glucose	0.00	2.30×10^{-2}	0.59	0.65	1.64×10^{-3}	3.85×10^{-3}
furfural	0.00	3.00×10^{-3}	0.00	0.00	6.20×10^{-2}	0.00
H_2SO_4	0.00	5.00×10^{-3}	0.00	2.19×10^{-3}	2.19×10^{-3}	5.14×10^{-3}
cellulase	0.00	0.00	1.24×10^{-3}	1.34×10^{-3}	1.34×10^{-3}	3.15×10^{-3}
LA	0.10	0.00	0.00	0.00	0.42	0.99
formic acid	0.00	0.00	0.00	0.00	0.17	0.00

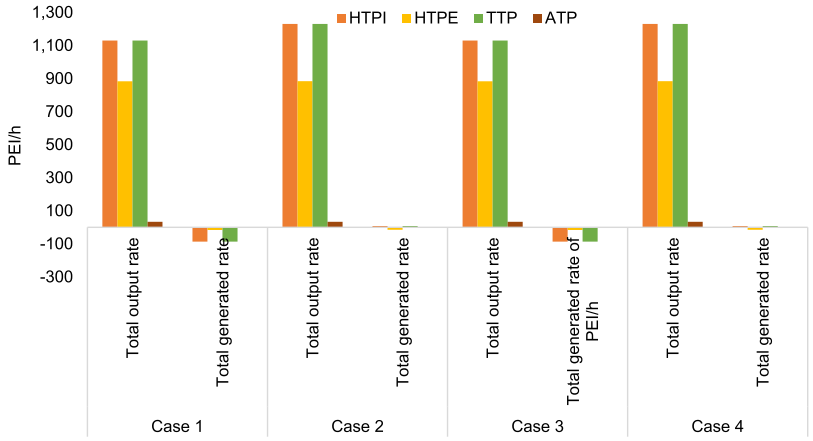


Figure 2. Rates of the PEI for toxicological categories.

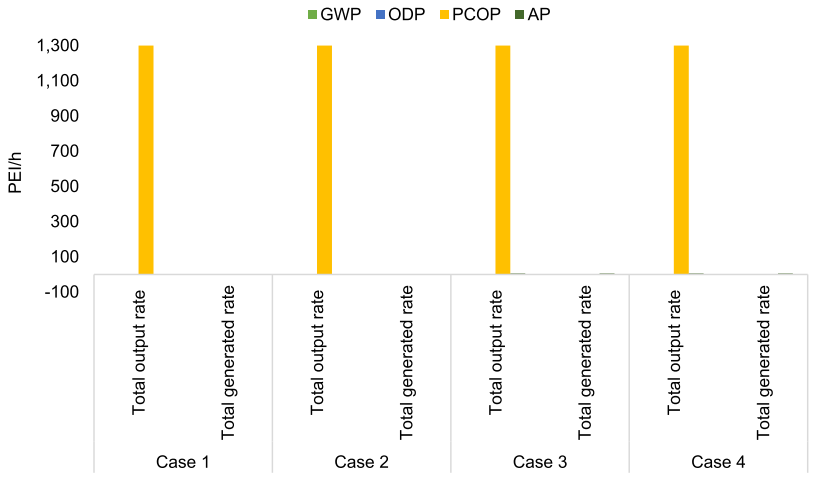


Figure 3. Rates of the PEI for atmospheric categories.

reducing sugars, is mixed with the catalyst (H_2SO_4) before entering the system. The second step is developed in a back-mix reactor which operates at 180 °C and 14.1 atm pressure. In this unit, HMF obtained in the first reactor, which is subsequently dehydrated to form LA and formic acid. Besides, xylose is also transformed into furfural.[22,23] The reactions and FYP of this system[24] are shown in eqs 2 and 3.

$$(\text{Glucose})_n \rightarrow n\text{H}_2\text{O} + \text{LA} + \text{formic acid} \qquad \text{FYP: } 0.80 \tag{2}$$

$$(\text{Xylose})_n \rightarrow n\text{H}_2\text{O} + \text{furfural} \qquad \text{FYP: } 0.50 \tag{3}$$

LA was obtained at 35.64 % wt, in the outlet reactor stream (AC-17). Therefore, in order to synthesize a product with commercial purity, the main flow is sent to a purification stage.

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This unit is composed of two distillation towers. In the first column, organic volatile compounds such as formic acid and furfural are removed from the LA mixture. It is worth mentioning that this design just considered generation of LA as the main product; therefore, if the biorefinery concept is applied, such byproducts can be potentially purified by using solvent extraction methods.[25] This process topology could produce three main products becoming into a biorefinery.[26] Otherwise, LA is obtained from the bottoms of the second column at 98.5 % wt. Finally, the main product is cooled to 28 °C and sent to storage [see DT-09]. A total flow of 38 392 TPA of LA was produced which represents a global feedstock to product yield of 29.10%.

Environmental Assessment of the ACD Process. For the modeled ACD process, environmental assessment was implemented based on the WAR. Extended material and energy balances obtained from process simulations permit estimating the potential environmental impacts (PEIs) for this process. Figure 2 shows the output and generated rate of the PEI for this case study. Results revealed that through this evaluated ACD topology, the amount of outlet impact is less than the quantities of these that enter the process. Negative values were obtained for generation rates of the PEI for case 1 and case 3, which report -1.89×10^2 and -1.83×10^2 PEI/h, respectively. Otherwise, cases 2 and 4 showed a generation rate of 1.67 and 8.01 PEI/h, respectively. This indicates that the main product stream influences the environmental performance of this design. From a global viewpoint, this process has an environmentally friendly performance. Figure 3 displays toxicological impacts generated and the output rate of the PEI for modeled synthesis of LA. The output rate of the PEI for human toxicity by ingestion (HTPI), human toxicity by dermal exposure (HTPE), and terrestrial toxicity potential (TTP) categories is moderate for all cases, while the aquatic toxicity potential (ATP) category remains in low values. The abovementioned finding implies that the potential effects generated by this process on aquatic systems are small.

Figure 5 shows the performance of atmospheric impact categories evaluated for this case study. This analysis is developed assessing global categories: global warming potential (GWP) and ozone depletion potential (ODP); regional categories: acidification potential (AP) and photochemical oxidation potential (PCOP). Atmospheric analysis shows that LA synthesis does not present important environmental concerns related to potential atmospheric/air pollution. For each evaluated case, PCOP was the most impacted atmospheric category. The abovementioned fact can be related to the use of organic compounds with concerns related to their volatility and chemical affinity with ethene which is the reference used to evaluated the PCOP category.

Safety Assessment of the ACD Process. ISI estimation was developed assuming the worst possible condition for each assessed subindex. This allows evaluation of unknown situations as the maximum associated risks that can be generated within a system. The inherent safety subindex for chemical substances was measured by eq 4.

The first and second terms in eq 4 are the enthalpy of formation of main and side reactions. These parameters in eq 4 are associated to measure the exothermic grade of reaction systems. For this process, main and side reactions were found in the ACD reaction. Table 3 shows safety subindexes by chemical reactions for this case study.

Table 3. Heats of Reaction for ACD

main reaction	$HMF + 2H_2O \rightarrow C_5H_8O_3 + C_2H_2O$	$\Delta H_o = 661.1$ kJ/mol[a]
side reaction	$C_5H_4O_4 + 2H_2O \rightarrow C_5H_8O_3 + C_2H_2O$	$\Delta H_o = -35$ kJ/mol[a]
$I_{rm_{max}}$	0	main reaction is endothermic
$I_{rs_{max}}$	1	side reaction is slightly exothermic

[a]Values estimated by authors.

$I_{int_{max}}$ refers to those chemical interactions derived from unwanted reactions between substances and materials in the plant area. For this case, the worst interaction is presented in the main reactor, with the mixture formed by formic acid and furfural. These substances have concerns according to the toxicological information available for such components. This criterion is evaluated based on the reported threshold limit value (TLV) for each dangerous substance. Thus, unexpected chemical interactions related to this potentially risky mixture are set for this system. Therefore, an $I_{int_{max}} = 2$ is assigned. An overall safety subindex for measuring dangerous chemical substances $(I_{fl} + I_{ex} + I_{tox})_{max}$ is developed to quantify potential inherent risk associated with flammability, explosivity, and toxicity of chemical substances. In the case of this process, sulfuric acid, furfural, and formic acid were identified as the most dangerous compounds. Table 4 shows the results for the dangerous substance safety index.

$$I_{ch} = I_{rm_{max}} + I_{rs_{max}} + I_{int_{max}} + (I_{fl} + I_{ex} + I_{tox})_{max} + I_{cor_{max}} \quad (4)$$

Table 4. Safety Parameters for Dangerous Substances

substances	sulfuric acid[a]	furfural[b]	formic acid[c]
flash point (°C)	N/D[d]	60	69
I_{fla}	0	1	1
UEL-LEL (v/v %)	N/D[d]	17%	39%
I_{exp}	0	1	2
TLV (ppm)	1	2	5
I_{tox}	5	4	4
$(I_{fl} + I_{ex} + I_{tox})_{max}$	5	6	7

[a]Data taken from ref 28 [b]Data taken from ref 29 [c]Data were taken from ref 27 [d]Not determined.

According to the properties reported in Table 4, it is worth mentioning that the assessed dangerous substances present a similar performance in their properties. In the case of flammability, sulfuric acid was assigned with an $I_{fla} = 0$, given the nonflammable feature of this substance. Otherwise, for furfural and formic acid, almost the same flash point is reported which ranges between 60 and 70 °C for both components. Toxicity for all three substances is quite similar considering reported TLVs for each of these. In terms of explosivity, the main difference between these substances is associated with formic acid that is a moderate explosive substance,[27] while furfural and sulfuric acid are not. For an overall evaluation of dangerous substance subindex, formic acid obtained the highest score. On the other hand, the corrosivity subindex evaluates the required construction material according to handling needs of substances. This parameter is directly related to the equipment safety subindex; therefore, it was established considering the requirements for equipment and processing units of the ACD

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Table 5. Description of Main Equipment Used for Modeling ACD Topology

equip name	type of equip	temp. (°C)	pressure (atm)	process unit	material
mixing	tank	28.00	1.00	PT	SS
pretreatment reactor	reactor	180.00	14.10	PT	Hastelloy/SS
flash cooler	shell tube	140.00	14.10	PT	SS
filter	filter/membrane	140.00	1.00	PT	SS
ion-exchange unit	separator	45.00	1.00	PT	SS/PP/RS-L
reacidification tank	tank	45.00	1.00	PT	SS
over-liming tank	tank	35.00	1.00	PT	SS
hydro-cyclone	rotatory-drum	50.00	1.00	PT	epoxy lined
filter-2	filter/membrane	30.00	1.00	AC	epoxy lined
mixing-1	tank	30.00	1.00	AC	SS
hydrolysis reactor	reactor	30.00	1.00	AC	SS
filter-3	filter/membrane	30.00	1.00	AC	SS
lignin precipitator	separator	30.00	1.00	AC	SS
mixing-2	tank	30.00	1.00	AC	SS
ACD reactor-1	reactor	210.00	24.67	AC	Hastelloy/SS
ACD reactor-2	reactor	180.00	14.1.0	AC	Hastelloy/SS
distillation-1	column	220.00	1.00	DT	SS
distillation-2	column	260.00	1.00	DT	SS

process. This was done according to operational conditions and extended mass and energy balances obtained by simulation, along with the process flowsheet diagram displayed in Figure 1. Table 5 shows a description of main equipment used for the the production process of LA. For this case study, corrosive substances such as formic acid, NaOH, or sulfuric acid are involved in different processing stages. Likewise, stainless steel (SS) is the most common material used for construction among evaluated equipment, with a use of approximately 72%. They suggest that acids and alkalis at diffeternt concentrations can be handled at various stages of this process.[30] Moreover, for a pretreatment reactor, Hastelloy c-200 was selected (along with SS), this alloy is composed of nickel, chromium, and molybdenum, and it is recommended for handling sulfuric acid.[31] Therefore, it was also assumed that this is the material used for ACD reactors, although it is important to mention that glass-based materials are also widely used for H_2SO_4 handling.[31] According to the abovementioned result, an $I_{cor_{max}} = 2$ was assigned taking into account that special materials such as Hastelloy, polypropylene (PP), epoxy lined, and resin-lined (RS-L) are required for some process equipment. All parameters needed for chemical substance safety calculation were determined; therefore, eq 4 was solved obtaining an $I_{ch} = 12$.

The second step of ISI calculation is related to the evaluation of the process inherent safety index. This parameter is measured by eq 5. The estimation of the PIS requires the knowledge of the operational conditions of the process because this metric considers maximum stress points through the system.

$$I_{PS} = I_I + I_{T_{max}} + I_{P_{max}} + I_{EQ_{max}} + I_{ST_{max}} \quad (5)$$

The first term in eq 5 is the inventory of the plant, this parameter measures the mass contained in any process equipment (tanks, reactor, and mixers, among others) for a hydraulic retention time of 1 h. In this plant equipment, reactors, tanks, separators, or heat exchangers were simulated. From a global viewpoint, a total inventory of 285 tones was calculated for the inside battery limits (ISBL). In this case, the outside battery limits (OSBL) were not considered because it was assumed that the main processing units belong to ISBL. This result represents a $I_I = 4$, which means that this system handles with great amounts of mass representing a stressing factor for the equipment and general safety of the plant. The maximum temperature in this process was found in the AC unit, specifically in the first reactor which is operated at 210 °C. Also, the maximum operational pressure (24.67 atm) for this unit was found. Table 6 shows the safety subindexes for inventory, temperature, and pressure estimated for this system.

Table 6. Safety Subindexes for I_I, $I_{T_{max}}$ and $I_{P_{max}}$

indicator	criteria	score
I_I	based on the inventory for ISBL	4
$I_{T_{max}}$	based on the maximum temperature of the process	2
$I_{P_{max}}$	based on the maximum pressure of the process	1

Another important parameter for process inherent safety calculation is the equipment safety subindex. The ISBL of the process represent an important number of equipment such as reactors, bombs, heat exchangers, storage tanks, separators, and filters, among others that for itself setting and design have intrinsic risks associated with the operations. This system considers the design of process units as storage tanks, filters, separators, ionic exchangers, distillation columns, reactors, and heat exchangers, among others. Based on equipment described above and features reported in Table 5, I_{EQ} is assigned according to the potential risks associated with the most dangerous operational equipment. In this case, the severity of pressure and temperature, and the specific purpose of each processing unit, pretreatment, and the ACD reactor along with distillation towers are identified as the riskiest equipment obtaining an $I_{EQ} = 3$.[32]

Finally, a secure structure subindex was estimated. This parameter is determined considering historical data and reports from heuristics and engineering experience of well-known processes. Yan et al.[33] reported that ACD is a process just developed under the semi-industrial scale through a recognized operation named "Biofine process". Therefore, this simulation was developed setting a large-scale processing capacity, but according to historical data reported for ACD, it is assigned as $I_{ST_{max}} = 2$. This value refers to novel or emerging large-scale processes.

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Globally, the ISI can be evaluated through subindexes calculated in this case study. Table 7 shows the ISI subindexes

Table 7. ISI Parameters for ACD

CIS	PSI	ISI
$I_{rm_{max}} = 0$	$I_I = 4$	$I_{ch} + I_{ps} = 24$
$I_{rs_{max}} = 1$	$I_{T_{max}} = 2$	
$I_{int} = 2$	$I_{P_{max}} = 1$	
$(I_{fl} + I_{ex} + I_{tox})_m = 7$	$I_{EQ} = 3$	
$I_{cor} = 2$	$I_{ST_{max}} = 2$	
$I_{ch} = 12$	$I_{ps} = 12$	

estimated for the ACD process. A global score of 24 was obtained with an equal contribution of 12 points for the CIS and PSI. The abovementioned result indicates that this process has a balanced performance for both safety categories, in fact operational conditions and thermodynamics of the reactions do not represent mayors concerns for the inherent safety of this process. Heikkila[12] suggested that for a typical or neutral safety performance of a chemical processing, an ISI score equal or below to 24 is generally reported. Considering above, this case study showed a total ISI equal to the recommended standard; thus, the modeled design for ACD exhibited a neutral safety performance.

CONCLUSIONS

This study presented an environmental and safety assessment for a large-scale ACD process. Results revealed that this process showed a balanced performance for chemical and process safety inherent indexes. Specifically, it was determined a score of 12 for both chemical substances and process inherent safety. Likewise, the ACD pathway for LA production from banana rachis showed an ISI performance within the recommended safety standards. The abovementioned fact might be an important finding because this analysis allowed establishing that this process (at large scale) is safe compared to the reference value. Otherwise, application of the WAR confirmed that the modeled process topology has an environmentally friendly performance, and even consumption rates of PEI for case 1 and case 3 were obtained. The abovementioned result indicates that environmental impacts regarding process energy sources do not affect the overall performance of the plant for both atmospheric and toxicological categories. Globally, PCOP was the most impacted atmospheric category, and this is explained by the presence of volatile organic compounds through the process. For future work is recommended to consider the evaluation of the presented ACD topology based on economic and energy parameters in order to get a wider vision in sustainability terms. Also, the application of the biorefinery concept which would consider commercial production of formic acid and furfural as products could be interesting for generation of performance comparisons.

METHODOLOGY

In this study, banana rachis is used as a precursor to produce LA via ACD. This chemical substance can be formed from different routes such as organic synthesis, reducing sugars synthesis, and direct furfuryl alcohol conversion.[5] The process design is performed through a computer-aided process engineering approach which requires process information such as material/energy balances, temperature and pressure conditions of each unit, and reactions yields, among others. The technical data required to perform process simulation are taken from the literature.[34,35] Process modeling and simulation allow obtaining extended energy and mass balances, mixing properties, and heats of reaction under defined process conditions and stages. These parameters are required to perform environmental and safety assessments of the process. Finally, such analyses are developed to diagnose potential improvement opportunities with the aim of screening a most suitable and sustainable design. Figure 4 shows the step-wise methodology applied for the evaluation of the ACD pathway for LA production.

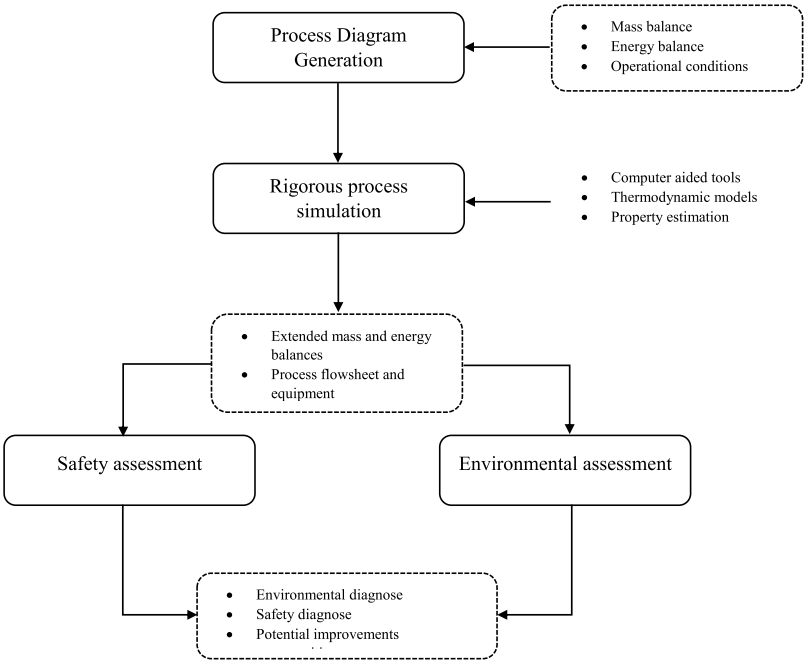


Figure 4. Process evaluation for the ACD process.

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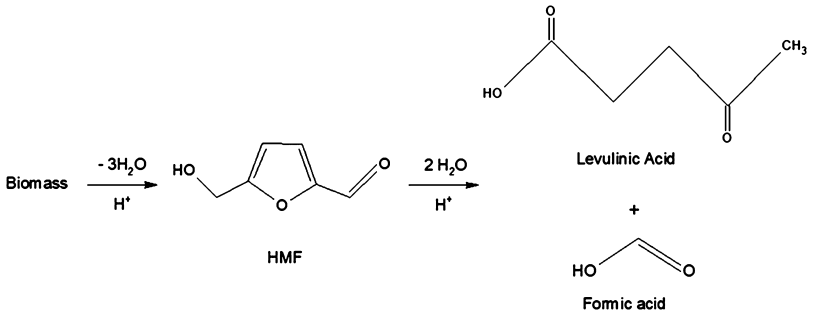


Figure 5. Reaction scheme for ACD.

Process Simulation. Process simulation and modeling require selecting chemical substances, an adequate thermodynamic model and state equation(s), setting processing capacity, and establishing input conditions such as mass and energy flows, temperature, pressure, reaction yields, and stoichiometry, among others.[36] In order to develop the simulation of the proposed ACD pathway for LA production, Aspen Plus software was selected. This computer-aided tool is widely used for simulation of existing and emerging chemical processes. This software has several components and substances incorporated in its enterprise database, so the majority of the needed compounds are available. For those components which do not exist in software database, authors used Aspen Property Estimator to create and estimate the physical−chemical properties of such components in the software. Most of the chemical and physical properties of these substances were obtained from the literature.[37] Aspen Plus requires introducing component properties such as boiling and melting points, molecular weight, thermodynamic properties, critical properties, and free energy of formation, among others. Nonrandom two liquids (NRTLs) were chosen as the thermodynamic-base model for process simulation and modeling according to their real representativeness for the estimation of polar/nonpolar mixtures and thermodynamic equilibriums.[38]

Production of LA via ACD of Banana Rachis. As described, there are two main ways to produce LA at the semi-industrial scale, the first is the organic pathway and the second is the acid-catalyzed pathway. The proposed process was developed based on the second route. The ACD reaction is the base technology for the production of LA proposed in this study. A processing capacity of 132 000 TPA of banana rachis was set as the mass inlet flow. This parameter was established according to the local availability of these residues in the north of Colombia. Lignocellulosic biomass has to be hydrolyzed in order to increase the availability of reducing sugars (C5 and C6) contained in the raw material structure. Therefore, the acid pretreatment stage was simulated considering operational conditions reported by Wooley et al.[19] After C6 and C5 extraction, the process uses the acid dehydration reactor. This stage is performed by using H_2SO_4 (1 M) as the acid catalyst according to experimental conditions and performances reported by Girisuta[39] and Kang et al.[23] Xylose and glucose flows are mixed along with the acid catalyst, for producing LA (from glucose dehydration), along with formic acid and furfural (from xylose dehydration) as byproducts.[40]

LA is produced from glucose in a reaction mechanism involving dehydration of a six carbon sugar to HMF. 5-Hydroxymethyl furfural which is subsequently rehydrated forming LA along with formic acid. On the other hand, xylose is dehydrated to form furfural. The reaction scheme for LA production is shown in Figure 5. The outlet reaction flow is sent to a cooling unit for reaching 30 °C. Thus, the cooled flow is sent to the purification stage which is composed of two distillation towers where LA is extracted, from the bottom of the second column, at a concentration of 98.5 % wt.[41]

Environmental Assessment. Several methodologies and tools to evaluate environmental performance and estimate impact assessment of emerging and existing technologies are reported in the literature. The LCA and Eco-Indicator 99, among others, are widely applied for this purpose.[42] The WAR is widely applied to develop environmental analysis by the estimation of potential impacts for the ACD pathway for producing LA from lignocellulosic biomass. The WAR method was developed by the US Environmental Protection Agency (EPA), this tool allows evaluating process alternatives by the assessment of eight environmental impact categories. These parameters are classified into toxicological and atmospheric aspects.[43] Toxicological categories are HTPI, HTPE, ATP, and TTP, while atmospheric categories involve evaluating parameters such as GWP, ODP, PCOP, and AP.[44] The output rate of the PEI is calculated by using eq 6, while the total mass output rate is calculated by using eq 7. The total generation rate of the PEI is estimated by using eq 8, and the total mass generation rate is determined by using eq 9. Therefore, $i_{out}^{(cp)}$ and $i_{in}^{(cp)}$ are the rate of the PEI exiting and entering the evaluated process because of chemical exchanges within the process, respectively. $i_{out}^{(ep)}$ and $i_{in}^{(ep)}$ are the rate of PEI leaving and entering the process associated to energy generation within the process, while $i_{we}^{(ep)}$ and $i_{we}^{(cp)}$ are the PEI leaving the process as a consequence of the release of waste energy associated to energy generation and chemical stages within the process. $M_j^{(in)}$ and $M_j^{(out)}$ are the input and output mass flow of the stream j, X_k is the mass fraction of a component k in the stream j, ψ_k is the overall PEI of chemical k, and P_p is the mass flow rate of the product P.[31] Figure 6 displays the diagram for balance of the PEI for a chemical process taking into account the contribution of energy generation. Such WAR equations (see eqs 6−9) are explained by the interactions[45] described in Figure 6.

The environmental assessment of LA production via ACD was performed from four case studies in order to determine the influence of energy and product streams into the output and generation rates of PEI for this process. The abovementioned fact allows determining improvement opportunities regarding energy consumption and these derived effects for a random discharge of substances (such as the product) into the environment. Likewise, case 1 is formulated considering only mass streams without product contributions. Case 2 considers mass and product streams without energy contribution. Case 3 is based on case 1 but taking into account energy streams. Finally, case 4 considers both energy and product stream contribution

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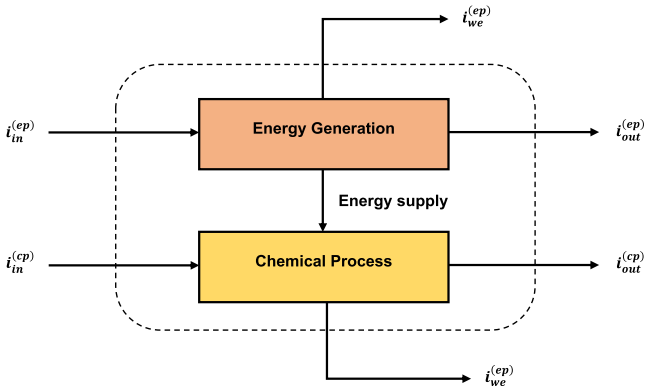


Figure 6. Balance diagram for estimation of the PEI by using the WAR.

along with all mass flows. The combination of global impact assessment, impacts by category, and analysis of effect derived from energy flows and sources allowed obtaining a holistic diagnosis of the modeled process from the environmental viewpoint.

$$i_{out}^{(t)} = i_{out}^{(cp)} + i_{out}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)} = \sum_{j}^{cp} M_j^{(out)} \sum_{k}^{cp} X_{kj}\psi_k + \sum_{j}^{ep-g} M_j^{(out)} \sum_{k}^{ep-g} X_{kj}\psi_k \quad (6)$$

$$i_{out}^{(t)} = \frac{(i_{out}^{(cp)} + i_{out}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)})}{\sum_P P_P} = \frac{\sum_j^{cp} M_j^{(out)} \sum_k^{cp} X_{kj}\psi_k + \sum_j^{ep-g} M_j^{(out)} \sum_k^{ep-g} X_{kj}\psi_k}{\sum_P P_P} \quad (7)$$

$$i_{gen}^{(t)} = i_{out}^{(cp)} - i_{in}^{(cp)} + i_{out}^{(ep)} - i_{in}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)} = \sum_{j}^{cp} M_j^{(out)} \sum_{k}^{cp} X_{kj}\psi_k - \sum_{j}^{cp} M_j^{(in)} \sum_{k}^{cp} X_{kj}\psi_k + \sum_{j}^{ep-g} M_j^{(out)} \sum_{k}^{ep-g} X_{kj}\psi_k \quad (8)$$

$$i_{gen}^{(t)} = \frac{i_{out}^{(cp)} - i_{in}^{(cp)} + i_{out}^{(ep)} - i_{in}^{(ep)} + i_{we}^{(cp)} + i_{we}^{(ep)}}{\sum_P P_P} = \frac{\sum_j^{cp} M_j^{(out)} \sum_k^{cp} X_{kj}\psi_k - \sum_j^{cp} M_j^{(in)} \sum_k^{cp} X_{kj}\psi_k + \sum_j^{ep-g} M_j^{(out)} \sum_k^{ep-g} X_{kj}\psi_k}{\sum_P P_P} \quad (9)$$

Safety Assessment. For unproven processes or adaptations of existing ones, many of the technical and economic decisions are strongly oriented by safety factors. Therefore, it is very important for engineers and designers to consider process safety in order to evaluate potential risks associated with the development of engineering projects and also the improvement of existing plants. This allows taking designs and operational decisions considering the mitigation of inherent risks of the evaluated process.[16] The ISI is a technique used to measure the inherent safety for chemical processes in conceptual design stages.[46] The ISI parameter is calculated by using eq 10 as follows

$$\mathrm{ISI} = I_{ch} + I_{ps} \quad (10)$$

I_{ch} is the inherent safety sub-index for chemical substances and I_{ps} is the PIS. The global assessment of the ISI is performed as shown in eq 10, considering the evaluation of the chemical substances and the process structure.

The first is determined from the contribution of parameters such as heats of reaction, toxicity, explosivity, and interaction chemistry of the chemical compounds involved in the process, while the second is determined from the parameters of the process such as temperature and maximum pressure, inventory, and process structure, among others. Table 8 shows the score and symbols for safety parameters.

Table 8. Scores and Symbols for the ISIs

I_{ch}	symbol	score
heat of main reaction	I_{rm}	0−4
heat of side reaction	I_{rs}	0−4
chemical interactions	I_{int}	0−4
flammability	I_{fl}	0−4
explosivity	I_{ex}	0−4
toxicity	I_{tox}	0−6
corrosivity	I_{cor}	0−2
I_{ps}	symbol	score
inventory	I_I	0−5
process temperature	I_T	0−4
process pressure	I_P	0−4
equipment safety	I_{EQ}	0−4 (ISBL)
		0−3 (OSBL)
process secure structure	I_{ST}	0−5

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02231.

Mass and energy balance for the pretreatment unit; mass and energy balance for the acid dehydration unit; and mass and energy balance for the distillation unit (PDF)

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Notes

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■ ABBREVIATIONS

TPA, tones per annum; LA, levulinic acid; HMF, hydroxymethyl furfural; ACD, acid-catalyzed dehydration; NRTL, nonrandom two liquid; PEI, potential environmental impact; EPA, Environmental Protection Agency; HTPI, human toxicity by ingestion;

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HTPE, human toxicity by dermal exposition; ATP, aquatic toxicity potential; TTP, terrestrial toxicity potential; GWP, global warming potential; ODP, ozone depletion potential; PCOP, photochemical oxidation potential; AP, acidification potential; ISCH, inherent chemical safety index; PIS, process inherent safety index; ISI, inherent safety index; FYP, fraction yield to product; WAR, waste reduction algorithm; TLV, threshold limit value; ISBL, inside battery limits; OSBL, outside battery limits

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