CHEMICAL ENGINEERING TRANSACTIONS

VOL. 80, 2020

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Eliseo Maria Ranzi, Rubens Maciel Filho

ISBN 978-88-95608-78-5; **ISSN** 2283-9216

DOI: 10.3303/CET2080047

Technical-Economic Analysis of Processes for the Production of Levulinic Acid

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Nowadays most of energy supply and chemicals are produced from fossil fuels. However, environmental concerns like global warming, depletion of non-renewable resources and pollution, force to search for more sustainable alternative feedstocks. In this framework, the valorization of renewable resources is currently one of the most promising strategies for the next future. In particular, the use of biomass is ranked first for production of chemicals. One of the most attractive compounds that can be obtained from lignocellulosic biomass is Levulinic acid (LA). The present work analyses, from a technical, economic and safety standpoint, the valorization of waste biomass (OPEFB, oil palm empty fruit bunch) to LA with different methodologies. Energy demand of the plant and the separation efficiency are evaluated carrying out process simulations by the commercial software Aspen HYSYS V10. The obtained results allowed an economic analysis of the alternatives, based on the evaluation of investment and main operating costs. The alternatives were screened on the basis of net present value (NPV) of costs. Safety performance was investigated by an inherent safety assessment method. This considered toxic dispersion and fire scenarios, calculating the damage distances associated with the potential outcomes of an accident and allowing for the evaluation of a potential hazard index for each main process equipment. The choice of the optimal layout configuration for the production of LA in early phases of design allowed to address, in a time and cost-effective way, further design activities in reducing the energy demand and ensuring potentially safer plants making the whole process more sustainable.

1. Introduction

Today, the research of new sustainable technologies that guarantee the production of chemicals and energy is a crucial challenge to combat global warming. Nowadays worldwide energy demand is mainly satisfied by the use of fossil fuels; however, the availability of this resource is decreasing and chemical processes that employ this raw material have proved to be less and less sustainable from environmental standpoint. As a consequence, the scientific community is turning its attention on renewable resources such as solar (Kim et al., 2019), hydro (Rubes et al., 2018), wind (Nazir et al., 2019) and biomass (Huang et al., 2019). In this perspective, one of the main achievements is to produce high-value-added biocomponents using biomass as a raw material replacing fossil fuels. However, these new sustainable methods must cope with lower energy efficiencies and higher transport and pre-treatment costs. In addition, it is necessary to underline the social competition problem with agricultural crops. The ethical and ecological results are achieved when the agricultural lands will be completely employed for the production of human food chain raw materials, while the chemical processes will specialize in using of waste biomass as feedstock. This is a key point for technological development. In this work the attention will be focused on specific processes for the valorization of lignocellulosic waste biomass in order to produce chemicals such as Levulinic Acid (LA), Formic Acid (FA) and Furfural (F). These value-added organic components can be obtained via hydration and dilute acid-catalyzed rapid hydrolysis of lignocellulosic feedstock. LA is proposed for a large number of applications (Ranzi et al., 2018) and thanks to its versatility, it is classified as one of the top twelve value-added chemicals from biomass feedstock. Nevertheless, its production on industrial scale is currently limited by the lack of detailed information for process design, the complexity of the separation of byproducts and the low reaction

Paper Received: 26 October 2019; Revised: 1 March 2020; Accepted: 12 April 2020
Please cite this article as: Tacchini E., Casson Moreno V., Tugnoli A., Cozzani V., 2020, Technical-economic Analysis of Processes for the Production of Levulinic Acid, Chemical Engineering Transactions, 80, 277-282 DOI:10.3303/CET2080047

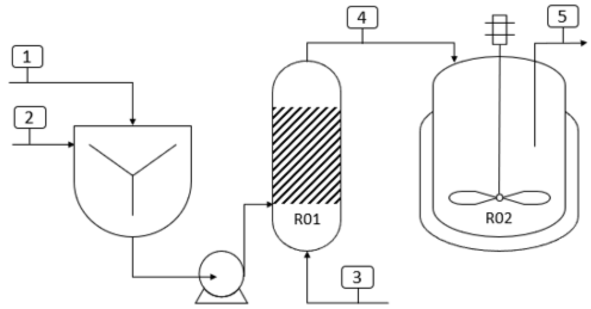
yields (Licursi et al., 2018). A successful conversion of biomass raw material is controlled by few important factors which are necessary for the overall process yield such as the thermodynamic reaction conditions, feedstock composition and separation performance. In this perspective, this analysis aims to offer a starting point of the process development for the production of Levulinic acid.

The purpose of this work is to provide a comparative assessment for production and separation technologies of LA. Several methodologies have been investigated in a preliminary literature analysis classifying them through production techniques, the different operating conditions and process yields. This activity allowed to identify a reference process for the production of LA: The *Biofine Process* (Fitzpatrick, 1997). The reaction scheme proposed by this technology, guarantees the maximum yield in terms of the amount of Levulinic and Formic acids produced thanks to its optimized process flowsheet and reaction conditions. The reaction products are mixed in a liquid solution which require a necessary separation section. This part of the plant is the most complex stage of the process due to the azeotropes that are generated by the reactions. In order to perform the separation stage several operations are required, and the optimization of the process flowsheet is a key point for the design of the plant. In this perspective, two separation schemes have been analyzed from economic, safety and environmental standpoint. Energy and separation efficiency of the proposed technologies have been evaluated carrying out process simulations with Aspen HYSYS. Flowsheets are analyzed in order to identify their optimal configuration, minimizing energy demand. Results of this simulations allow to estimate the major operating costs of the processes which are recombined with the investment costs in the determination of the Net Present Value (NPV) of the costs for the two alternative schemes. This is an economic performance indicator of the incidence of costs based on a pre-established time frame. The comparative interpretation of different NPV declares the most efficient initiative from economic standpoint. This evaluation has been integrated with a preliminary safety analysis for the determination of Inherent Safety Key Performance Indicators (KPIs) which allow to compare first each individual equipment and then the two entire processes considered. The results obtained allowed to identify the process alternative with lower overall costs and higher safety performance. In conclusion, this comparative study provides a general overview of the process from the reaction to the separation stage with the aim of introduce and investigate selection criteria for the next conceptual design phase.

2. Methodology

2.1 Definition of process reference scheme

The Biofine process is a recent technology for the production of Levulinic acid. This methodology is currently being studied on a laboratory scale and in pilot plants in order to investigate the best operating conditions for the conversion of biomass. The process consists of three principal equipment set up in series. The first one is a Pre-mixer where the lignocellulosic shredded biomass is supplied by rotary valve and added with inorganic acid solution, typically dilute sulfuric acid (SA, 4.8 wt%), to break down the organic macrocomponents of the biomass in the compounds that will participate in the subsequent reaction stage. The acid solution is supplied to a plug flow reactor (PFR) along with high-pressure steam. This equipment is operated at 210-220 °C with a residence time of 12 seconds in order to hydrolyze the cellulose and hemicellulose fractions to their soluble intermediates as Furfural and Hydroxymethylfurfural (HMF). The outflow from this first reactor is sent to a continuous stirred-tank reactor (CSTR) operating at 180-200 °C with a residence time of 1200 seconds. In this second equipment, the hexose intermediates are converted to LA and FA. The acid mass fraction is about 2 wt% in both the reactors. However, two side reactions lead to formation of Tar reducing the yield of main products. This complication lays the introduction of a filter-press unit in order to remove solid byproducts. A schematic representation of the reaction stage studied is presented in Figure 1.

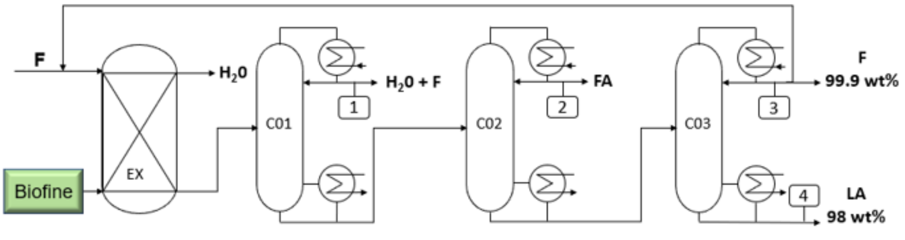


[t/d]	1	2	3	4	5
Biomass	2000	-	-	600	600
LA	-	-	-	-	560
FA	-	-	-	-	240
Furfural	-	-	-	320	260
HMF	-	-	-	750	-
Tar	-	-	-	-	310
SA	-	105	-	105	105
Water (l)	-	2100	-	3330	3030
HP steam	-	-	900	-	-

	R01	R02
P [atm]	25	10.5
T [°C]	215	190

Figure 1: Schematic representation of the Biofine process for the production of Levulinic acid adapted from (Casson Moreno et al., 2019).

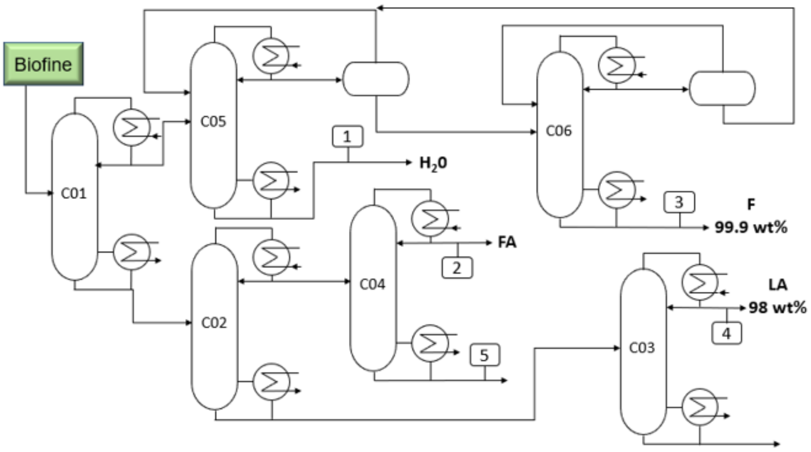
Operating parameters of the second reactor are chosen theoretically such that FA and Furfural vaporize, but some laboratory and pilot-scale tests are necessary in order to evaluate the possible decomposition of Formic Acid with the presence of Sulfuric acid. The reaction scheme has been improved compared to literature's technologies (Karthik, 2013) carrying out material balances and process simulations. Even with these improvements, Furfural and Formic acid formed in R02 do not completely vaporize as claimed and a small quantity of LA is lost. The reaction stage is followed by a downstream process for streams purification. The separation section requires several equipment in order to guarantee products at their commercial grades (Nhien et al., 2016a). Two different configurations have been considered to perform this operation, Figure 2 and 3 show the two processes flowsheet analyzed. Temperatures and Pressures are referred to the bottom conditions of the columns.



[t/d]	1	2	3	4
LA	-	-	-	540
FA	190	40	-	-
Furfural	154	25	8910	14
Water	276	1	-	-

	EX	C01	C02	C03
P [atm]	1	1.2	1.1	1.1
T [°C]	25	162	163	249

Figure 2: Process flowsheet of the Alternative 1 for the Downstream and Purification section adapted from (Nhien et al., 2016b)



[t/d]	1	2	3	4	5
LA	-	-	-	540	-
FA	210	12	-	-	8
Furfural	10	-	250	-	-
Water	2695	218	-	8	182

	C01	C02	C03	C04	C05	C06
P [atm]	1.2	1.1	0.1	1.1	3	1.1
T [°C]	112	150	217	100	100	160

Figure 3: Process flowsheet of the Alternative 2 for the Downstream and Purification section adapted from (Karthik, 2013).

Both alternatives mainly base separation efficiency on the different volatility of the system components. Therefore, in order to perform the downstream process, several distillation columns are employed. The first scheme involves a preliminary liquid-liquid extraction with furfural itself in order to remove water from stream of the reaction products increasing the concentration of LA and FA before the distillation column C01. The second alternative foresees a higher number of distillation columns. In order to increase C05 and C06 performances, these equipment are coupled with decanters which contribute to separate Water from Furfural.

2.2 Data gathering and process simulation

A comparative analysis of the two Levulinic acid separation methodologies has been carried out. Different points have been evaluated in order to investigate the best configuration for possible industrial-scale development. Some preliminary considerations are introduced to guarantee the same LA production and purity for the two schemes. Carrying out material balance and hypothesis on reaction yields, the conversional scheme of biomass has been improved compared to what is considered in literature (Karthik, 2013). More in detail it has been evaluate also the dehydration of glucose which promote the formation of HMF in the first reactor. Globally the processes guarantee a production of 540 t/d of Levulinic acid at its commercial grade of 98 wt%. The separation efficiency has been modeled through processes simulation by the commercial

Software Aspen HYSYS V10. This analysis allows to identify streams characterization and energy required to accomplish the separation stage. The lack of detailed data didn't allow to achieve in process simulations the same purity of the by-product Formic Acid stream as reported in the literature. However, the expected impact of this approximation on energy balances, and therefore on economic evaluations is minimal. Results obtained are necessary inputs for the economic evaluation and the preliminary safety analysis.

2.3 Economic evaluation and preliminary safety analysis

The developed economic assessment is based on the evaluation of the main fixed investment and operating costs. It has been edited an equipment lists for the two alternatives and determined an approximation for the installed costs of the principal equipment by exponential and Guthrie methods (Guthrie, 1969). It has been considered that the reaction stage is similar for both processes and, therefore, also the relative cost. Instead, it has been hypothesized that the principal operating cost are associated to the energy consumption, determined by the previous process simulations. The economic comparative analysis is concluded by the evaluation of Net Present Value (NPV) of the costs for each alternative as showed in Eq(1). It allows to decree the most cost-effective technology for LA production and separation. Cash flows ($A_{cf,i}$) are based on 10 years of the plant's useful life (n), 2 years for the construction (m) and a discount rate (i_r) equal to 10 %.

$$NPV = \sum_{i=0}^{m+n} \frac{A_{cf,i}}{(1+i_r)^i} \tag{1}$$

The economic assessment study has been integrated with a preliminary safety analysis with the purpose of the evaluation of impact areas associated with hazardous substances releases. The technique adopted involves the simplified application of a literature methodology (Tugnoli et al, 2007). In according to the methodology, the first step is the identification of the equipment present in the process and the related operative conditions such as pressure, temperature, substance involved and hold-up. Subsequently, a set of credible critical events, referred to as Losses Of Containment (LOCs), is assigned to each Process Unit. In this phase, some simplifications have been introduced: from the whole LOCs set it has been chosen a reference release scenario for each stream. In this perspective, to maintain conformity in the results and be able to draw objective conclusions, the same release of the entire mass flow for a duration of 3 minutes has been considered for all the main streams. In the evaluation of the safety performance of each distillation columns, are evaluated separately the distillate and the waste streams, while for the reaction stage the reference release has the equipment outflow composition. At that point the methodology introduces a bow-tie diagram in order to define both the direct causes leading to the critical event and the resulting dangerous phenomena. However, based on the characteristics of the substances and on the working conditions of equipment it has been considered that the pool fire and the toxic dispersion are the most likely final incidental scenarios that may occur. The major accidents develop from an uncontrolled liquid release which initially generates a puddle with a fixed mass. In particular, it has been approximated the mass as a product of the stream's weight flow and the duration of the release. Formic acid and Furfural are potentially toxic and flammable, while Levulinic acid has only flammability characteristics. Based on preliminary considerations it has been hypothesized to choose an incidental reference scenario for each equipment and simulate its development using the commercial software Aloha. The goal of these simulations is to predict the damage distance (h_j [m]) for each considered release. For fire modeling the damage threshold has been set at 7 kW/m^2 while for toxic dispersion at mixture IDLH of the released leakage, threshold values for irreversible damage (Scarponi et al, 2016). The comparative safety analysis is subsequently developed through the evaluation of Inherent Safety Key Performance Indicators (KPIs) as required by the applied methodology. In particular, for each equipment it has been calculated the Unit potential hazard index UPI_i [m^2] as shown in Eq(2) in order to quantify the threaten area of each release. In conclusion, for the two alternatives it has been determined the Overall potential hazard index PI [m^2] as shown in Eq(3) which gives, even approximately, a globally overview of the plant's damage area. The highest safety performance is achieved for lower PI index.

$$UPI_i = h_j^2 \tag{2}$$

$$PI = \sum_{i=1}^{n,equip.} UPI_i \tag{3}$$

3. Results and discussion

In Table 1 are reported the principal results obtained. The two compared processes have the same potential production and Levulinic acid purity, but they require different investment and operating costs. In particular, the first alternative needs a lower initial investment capital compared to the second one (respectively 23.7 M€ and 30.8 M€). However, the second scheme require lower energy costs in order to perform the separation stage (respectively 45 M€ and 33.9 M€). These results are obtained by considering both the overall thermal power required for the two purification sections (respectively 102 MW and 137 MW) and the costs of the necessary thermal vectors which depend on their temperature. Therefore, both alternatives present some advantages in this economic assessment making them potentially attractive. In this perspective, it has been considered the NPV of the costs as an indicator of the economic performance for the two schemes. The second alternative minimizes the overall money required, guaranteeing about 20% of costs saving. This preliminary assessment has decreed the economic advantage in the use of the second scheme in order to execute the downstream and separation section.

Table 1: Plant potential and principal results of the economic evaluation and preliminary safety analysis

	Alternative 1	Alternative 2
Biomass feed	2000 t/d	2000 t/d
LA produced	540 t/d	540 t/d
LA purity	98 wt%	98 wt%
Capital costs	23.7 M€	30.8 M€
Operating costs	45 M€	33.9 M€
NPV of the costs	274.1 M€	218.5 M€
PI	7.1×10^6 m^2	2.7×10^6 m^2

In the same table, the results obtained through the preliminary safety analysis are also listed. Aloha simulations have shown a clear difference for the threaten area from toxic rather than flammable substances releases. While the damage distance for pool fires assume in all cases values approximately around 10 m; for toxic dispersions varies in a range between 100 and 1000 m. This huge gap between the two considered scenarios makes the fire effect negligible compared to toxic events. Figure 4 shows the UPI_i of the main equipment which are, for each case, lower in the second alternative (with the exception of the two reactors that are the same for each scheme). For this reason, the overall potential hazard index PI is significantly lower for the second flowsheet (respectively 7.1×10^6 m^2 and 2.7×10^6 m^2). The first scheme, unlike the second, introduces a huge quantity of Furfural to perform the extraction of LA and FA. This solvent is present in all the distillation columns making them potentially dangerous. In addition, the Unit potential hazard indexes for columns C01, C02 and C03 of the first scheme assume almost the same values. This is a direct consequence of a series layout where the furfural outflow stream is on the last column, so each equipment has the same Furfural hold-up. Instead the extraction section (EX) is less worrying for these safety considerations; its operating temperature is near to the atmospheric one, so the evaporation of the puddle has less driving force due to the formation of the toxic cloud. Therefore, hazard indicators of each equipment globally assume lower values in the second alternative. Moreover, the second scheme optimizes the process layout: the parallel disposition of the columns C02 and C05 promote an efficiency subdivision of dangerous substances. Indeed, this arrangement minimizes the number of equipment in which toxic components are present guaranteeing lower levels of danger for columns in which Furfural is absent as C02 and C03.

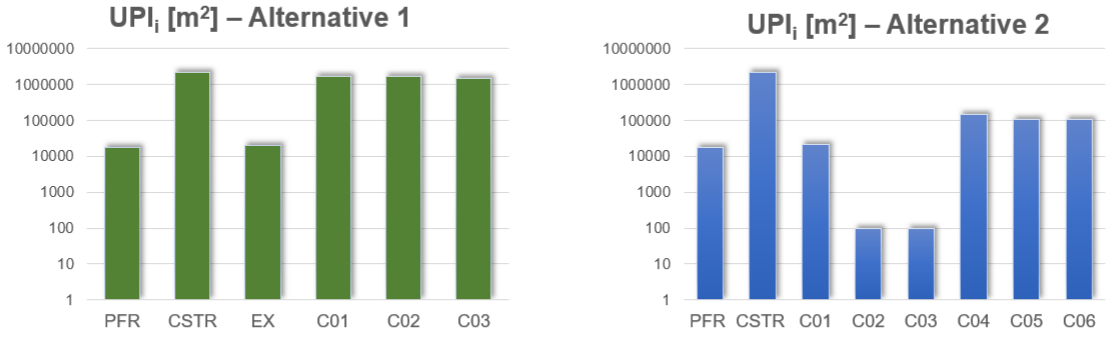


Figure 4: Unit potential hazard index of the main equipment in the two alternatives

4. Conclusions

This work presents a technical-economic analysis of main processes for the production of Levulinic acid from oil palm empty fruit bunch waste biomass. The Biofine process is a developing technology currently being studied mainly through some pilot plants. The efficiency of the process lies in the high yield it can guarantee; however, it still requires several researches on the complex separation mechanism. This work presents two plausible different alternatives for the downstream and purification section. Through the evaluation of economic and safety indexes a comparison of the two alternative schemes has been carried out, decreeing which is the best design configuration. In particular, the second scheme which use only distillation columns for the separation of LA, guarantees 20% of overall costs saving and reduces the threatened area by 62%. In addition, the economic advantage of this process layout lies in the low energy operating costs which is a fundamental parameter for determining the quantity of CO_2 emitted to produce that energy. Even in sustainability aspects and ecology footprint the second alternative proves to be more attractive.

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