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Simulation and Feasibility Evaluation of a Typical Levulinic Acid (LA) Plant using Biomass as Substrate

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Several problems has been worried the world population when it comes to sustainability subject. The imminent depletion of fossil fuels and the lack of alternatives to replace compounds produced by oil also add to this account . Countries that have their economy based on agribusiness (like Brazil) have a slight advantage in this scenario since naturally much of biomass is lost in the environment until the final product exportation takes place. It means that such biomass can be used in the production of several alternative fuels and other basic chemicals such as second-generation bioethanol and levulinic acid, diminishing the reliance on oil. This last one is a promising building block molecule an organic compound, intermediate in the synthesis of various chemical compounds for additives of fluids, fragrances, oils, plastics among others. Thus, in the present work, a complete simulation of levulinic acid production process from the acid hydrolysis of biomass (it was used sugarcane bagasses as an example) was conducted to produce 8 kilotons of levulinic acid per year (with high concentration of the final product (99,6 wt %)). Specifically, a generic large scale levulinic acid plant was performed using ASPEN PLUS® V.7.3. The main goal was to evaluate feasibility of the overall process using a typical production value based on actual plants (more specifically the Caserta plant, located in Italy). Despite of similarity of another works presented in open literature, a detailed discussion from the data obtained was carried out. Furthermore, a formic acid separation from water was fulfilled using activated charcoal adsorption become the whole process more sustainable in the near future.

1. Introduction

The dependence of the global economy on the utilization of fossil fuels has increased rapidly in the last 4 decades, accounting for 80,9% of the total energy production in 2006 (Koh and Ghazoul, 2008). The fossil resources have been consumed to fulfill the population energy needs that includes mostly transportation fuels and modern products manufacturing such as textiles, lubricants, fertilizers and polymers. In general, it is not difficult to say that a major part world's progress was based in a fossil fuel platform. However, these mineral resources have many disadvantages, such as: limited reserves, environmental damages and direct responsibility for global warming (Nhien et al. 2016). In fact, one of the greatest challenges that industry faces in 21st century is the transition from a "fossil fuels economy" to one based on renewable resources with various economic and environmental benefits: 1) reduction of the carbon footprint of chemicals and vehicle fuels; 2) a more profitable agricultural economy; and 3) the substitution of existing products by alternatives that are safer and have reduced environmental carbon footprint (Sheldon, 2011; Isikgor, 2015; Titirici & Pileidis, 2016).

In this sense, biofuels and other compounds from biomass (which consists of all forms of organic matter available in nature) have been presented as key factors to reduce the reliance on oil. They are considered as a renewable and infinite resources, since their production usually comes from agricultural crops. In addition, the substitution of petroleum derivatives could reduce greenhouse gas emissions since biomass is originated as part of the photosynthesis process, in which the energy of the sun is captured and transformed into sugars

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(Pereira & Ortega, 2010).These sugars can be burned to produce energy. In most cases these alternative sources are said to be renewable because the CO_2 emitted to the atmosphere is recaptured by the crop that will grow in the next cycle.

Therefore, in the present study, the compound **L**evulinic**A**cid (LA also known as 4-oxypentanoic acid or γ-ketovaleric acid) is highlighted. This acid was classified by the US Department of Energy as one of the 12 most promising building-block molecules in nature. Such molecule is considered an organic compound intermediate in the synthesis of various chemical compounds as additives for fluids, fragrances, oils, plastics and pharmaceutical compounds such as methyl tetrahydrofuran (MTHF). This occurs because levulinic acid contains ketones and carboxylic acid groups. These two functional groups are particularly important to produce a large number of chemical compounds, such as gamma-valerolactan (GVL), acrylic acid, 2-methylhydrofuran among others (Isikgor and Becer, 2015; Serrano-Ruiz et al., 2011; Lange et al., 2009).

As mentioned above, levulinic acid can be obtained from Biomass which has almost no costs. Considering that the largest biomass sources available contain lignocellulosic material (cellulose present in the leaves and trunk of the plants) whose hydrolysis (breaking) is hampered in detriment of the β-1,4 bonds present, there is still a great difficulty to produce biofuels on a large scale through lignocellulosic biomass. Biofuels (among other compounds produced via the fermentation route) have serious difficulties related to temperature and enzymes consumption. Levulinic acid, on the other hand, has the advantage of having purely chemical production routes, which, in turn, does not involve the use of microorganisms or present any limitations regarding temperature. Addressing more specifically the inherent conversion of biomass to levulinic acid, the first step is the hydrolysis of cellulose into glucose monomers followed by dehydration of glucose to hydroxy-methyl-furfural (HMF). Under acid conditions, the hydrothermal process allows the effective conversion of d-glucose into HMF. Levulinic Acid is produced through the hydrolysis of HMF under acid conditions also. In the acid-catalyzed conversion of hexose sugars into levulinic acid, **F**omic**A**cid (FA) is coproduced as a low-value chemical used in the production of formaldehyde, rubber, plasticizers, pharmaceuticals, and textiles(Lewkowski, 2001; Titirici & Pileidis, 2016).

The demand for levulinic acid has increased in recent years, being the annual demand around 3 kilotons. Only the MTHF (methyltetrahydrofuran) derivative may face a demand for levulinic acid of 20 kilotons by 2020 (Grand View Research, 2014). However, on the industrial scale, levulinic acid is available in insufficient quantities and produced by a process with difficulties to meet environmental standards (Titirici & Pileidis, 2016). In addition, their high price still makes their competitiveness unviable towards to oil-based intermediaries as there are still few industries.

Based on this information the main goal of this work was to evaluate the feasibility, bottlenecks and some process alternatives for a LA production in industrial scale of 8 kilotons/year. For this reason, process simulations were carried out employing ASPEN PLUS® V.7.3 software. Analysis of energy consumption in distillation columns, sustainability and catalyst consumption (H_2SO_4) were performed aiming to produce LA above 99% purity. As a secondary objective formic acid was produced at high concentrations (about 95 wt %) considering a possible increase in the plant profitability. Generally speaking this study is relevant because there is a lack of knowledge about the great potential of the use of levulinic acid as well as studies directed to its production in large scale. The conceptual idea of this work is to show some structural results based on what is currently presented by industry worldwide.

2. Description of Simulation of a Levulinic Acid (LA) commercial scaleplant using ASPEN PLUS® V.7.3 software

The material and energy balances as well as flow rate information of LA production process were generated using Aspen Plus process simulation software packages. The overall flowsheet of LA process is shown in Figure 1 (the picture was divided into two parts to improve the understanding of the process) and was based on Gaudereto et al. (2017) assumptions and simulations.

Basically, the simulation has a sugarcane bagasse feed (secondary biomass of sugar extraction from sugarcane) as its raw material, and water which was heated and pressurized to150 ºC and 8,6 bar to then be introduced into a CSTR reactor where the reactions effectively take place. In was added the catalyst in the CSTR reactor which consisted in sulfuric acid (H_2SO_4) at the same pressure and temperature of water stream. The purpose of the acid is to hydrolyze polysaccharides in sugar monomers in order to convert the monosaccharides to levulinic acid subsequently. Cellulose conversion in the reactor was obtained with 98 mol %, and the yields of levulinic acid (LA) and formic acid (FA) were 0.56 and 0.54 mol/(mol cellulose), respectively. In this study, to simplify the convergence, the sugarcane bagasse was approximate having only cellulose. Furthermore, another important specification was towards the sulfuric acid, which was conducted and diluted along the process to present a concentration no higher than 50 wt %.

After leaving the reactor, the mixture flow which carries the levulinic acid was intended to be separated and concentrated as much as possible. The first step to perform this operation was removing the solids present in this stream, which were, in this case, unreacted cellulose and HMF. For this reason, a filter (B1) was used to perform this initial separation and then the LA concentration process was carried out by a series of distillation columns. The first distillation column (B2) was used to separate sulfuric acid from the main flow entering in the column. The stream containing mostly acid was then directed back to the beginning of the process after been cooled in the mixer (B5). In the second distillation column (B12) occurred the separation between levulinic acid and water which leaves the top of this column in stream 33. This water carries a significant amount of formic acid and for this reason an alternative process using adsorption by activated charcoal was performed to recover it (formic acid from water). The third distillation column (B14) acts concentrating the final mixture to a commercial purity level (99.6 % m/m) presenting a mass flow of 919.65 kg/h of such product in LEV-ACID stream. On the other hand, the top product of the third column was sent back to the beginning of the process since a significant amount of levulinic acid is still there.

It must be highlighted that pretty much nothing was disposed along the process. Another important data was that the cellulose feed mass flow and the *make-up* sulfuric acid feed flow was, respectively: 2425 Kg/h and 16 kg/h.

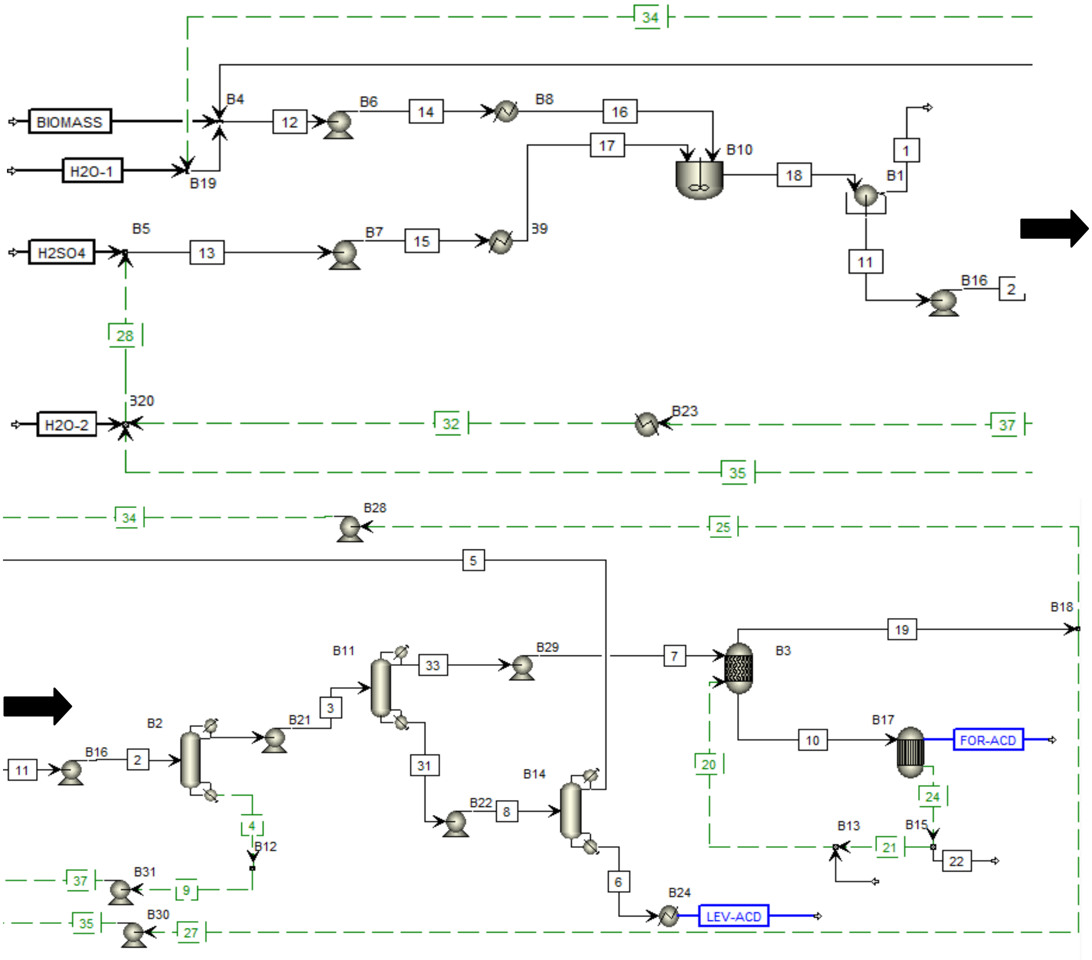

Figure 1: Schematic flowsheet of continuous levulinic acid manufacturing process. Biomass, H_2SO_4, H_2O streams are the raw materials and LEV-ACID and FOR-ACID are the streams products. At the top of the figure are the reactor and the recycle streams that return to the beginning of the process been B10 the reactor block. In the lower part the steps of separating and obtaining the final product are presented. B12, B11 and B14 are the distillation columns.

2.1 Kinetics and Thermodynamic approach

Regarding kinetics and process reactions, according to Gaudereto et al. (2017), these were modeled as classical variations of the pseudo-first-order Ahrrenius equations (Climent et al., 2012). In addition, some

important considerations/simplifications involving the reactions deserve to be highlighted: a) All glucose that is formed is produced by the glucans decomposition b) Due to its high decomposition rate, the concentration of HMF in the medium is always very low. What can be taken as true within the context of this work (Girisuta et al., 2006) c) The only parallel and undesired reaction occurs to form humins (Girisuta et al., 2013).
Regarding to the thermodynamics models, activity coefficient on the liquid phase was calculated by NRTL (Non-Random Two-Liquid) model. The non-idealities of the vapor phase were neglected assuming the activity coefficient is prevailing in such scenario.

3. Results and Discussion

Simulations were carried out considering the already existing production processes (among them pilot plants and commercial scale plants).In this way part of the simulation was based on Biofine technology, sulfuric acid mixed with biomass feeding them into two reactors operated in series at 210–220°C and 190–200°C, respectively (Fitzpatrick, 1997). The amount LA produced in the simulation developed in this work was based on GFBiochemicals production capacity recently reported. The company started LA production in 2009 in a pilot plant facility with a production capacity of 2000 metric tons per year in Caserta, Italy. In 2015 GFBiochemicals announced the start up of a commercial scale production plant, objectifying to produce up to 8,000 kilotons of LA per year by 2017 (Titirici & Pileidis, 2016). The operation temperature and sulfuric acid concentration were based on Gaudereto et al. (2017) work where several sensitivity analyses were performed through simulation. The authors concluded that the reactor should operate at low temperatures (150ºC) to reduce the formation of humins and in high concentrations of sulfuric acid to favor the production of glucose and HMF. The lower temperature of 150 ºC is part of Chang et al. (2007) study which stated that temperatures between 150°C and 230°C can increase the conversion of lignocellulosic materials to levulinic acid. High concentrations of sulfuric acid also positively influence conversions to levulinic acid, however, care must be taken. Although these hydrolysis reactions are effective in higher concentration, the mineral acid is harsh and corrosive, promoting equipment degradation. In this regard, a concentration near 50 wt% could provide a good conversion into LA not requiring corrosion-resistant and therefore more expensive pipeline (Gaudereto et al., 2017). The simulation considers the use of sugarcane bagasse. Brazil is one of the largest producers of sugarcane in the world. The bagasse, which remains after sugar extraction, is abundant and is currently used as a heat source for aquatubular boilers. However, several studies have focused on a more noble use for this biomass source as the second-generation ethanol and the production of levulinic acid.

Table 1: Results of mass flow and mass fraction of the main currents and products of process

Streams	**3**	**4**	**31**	**33**	**5**	**LEV-ACD**	**FOR-ACD**
TemperatureºC	99	274	255	99	235	25	25
Pressure bar	1	1	1	1	1	1	1
Mass Flow kg/hr	47343.9	2538.5	960	46383.9	40.35	919.65	383.03
H_2O	45985.44	1.50E-13	0.021	45985.40	0.021	4.50E-20	19.57
H_2SO_4	1.60	2505	1.60	0.00017	0.0012	1.60	0.000171
LEV.ACID	952.06	1.987	942.90	9.168029	26.85	916.05	0
FOR.ACID	367.09	1.40E-13	0.00058	367.09	0.00058	2.60E-18	363.45
Mass Frac							
H_2O	0.97	5.91E-17	2.20E-05	0.99	0.00052	4.90E-23	0.051
H_2SO_4	3.38E-05	0.98	0.0016	3.69E-09	3.08E-05	**0.0017**	**4.47E-07**
LEV.ACID	0.02	0.00078	0.98	0.00019	0.665378	**0.996**	0
HMF	7.48E-06	1.96E-06	0.00036	1.34E-08	0.000164	0.00037	0
FOR.ACID	0.0077	5.50E-17	6.12E-07	0.007914	1,46E-05	2.83E-21	**0.948**

Table 2: Results of the main energy consumption blocks (in kW) of the simulation.

Heat Exchangers utilities			**Distillation Columns utilities**			**Reactor utilities**		
Block	**Hot (kW)**	**Cold (kW)**	**Block**	**Hot (kW)**	**Cold (kW)**	**Block**	**Hot (kW)**	**Cold (kW)**
B8	7218		**B2**	32669.8	-35669.4	**B10**	2585.6	
B9	482.7		**B11**	32013.8	-31921.3	**B3**		-3173.4
B23		-178.5	**B14**	-65.1	65.2	**B17**		-837.4
B24		-131.5						

Table 1 shows the main results of process simulation. The streams were presented in terms of mass flow and mass fraction. Through them can be verified that the final concentrations of levulinic acid and formic acid are both marketable. Here, it is important to stress out the high concentration achieved for levulinic acid (99.6 wt%).

Table 2 shows the plant energy consumption data divided into hot and cold utilities. These data are also discriminated as: heat exchangers, distillation columns and process reactors. From this table it can be noticed that there is a potential for energy integration between heat exchangers. However, the energy integration would not meet even part of all the process energy requirement. Considering this context, the energy integration was left aside for now. Still in Table 2, it can be observed that the distillation columns (B2 and B11) present most of the energy consumption of the whole process both in hot and cold utilities. The unit of energy expenditures of each column are comparative to the bioethanol production industry. According to Ponce et al. (2015), simulations designed to produce 700,000 l/day of hydrous ethanol with a minimum top concentration of 92.6 wt% ethanol from an initial ethanol-water mixture of 8 wt% ethanol consumes in average 40 kW on the column reboiler. Despite the differences in the amount produced, relative volatility and the difference between the initial concentrations (in the present work the levulinic acid has 2 wt% when it is enter in the first column), the energy expenditure data corroborates mainly because the amount of water separated in both processes were similar.

Back in Table 1 it can be noticed a large amount of water circulating in the separation process (streams 3 and 33). These water streams correspond to the largest mass flow rate in the process. Likewise, these streams are the main consumer of hot and cold utilities in the distillation columns due to the successive evaporations and condensations. Water can be seen as a major contributor to energy consumption because, besides being present in high amounts inside the process, its separation from the compounds of interest is mandatory. In addition to this, water has a high heat capacity so its separation always demands a high amounts of energy. Thus, it would be interesting in future works to search alternatives to distillation in order to separate the levulinic acid from the aqueous solution by using less energy.

Regarding the catalyst (H_2SO_4), its insertion at low quantities is necessary to the process and it is provided by a *makeup* stream (approximately 16 kg/hr). Most of the losses of H_2SO_4 are located in the product streams (LA and FA) and in the filter after the reactor, however, this amount is low compared to the amount of LA and FA produced (916 and 363 kg/hr, respectively). Despite of the filter stream residue (which is intended to retain solid compounds that could eventually enter the distillation columns) the process does not generate any waste. Process efforts were intensified around the catalyst recycle stream (H_2SO_4) and water (H_2O) stream in order to avoid water and sulfuric acid losses or improper disposal. A major concern of the simulation was cause minimal environmental impact. Based on the simulation results presented, it can be said that the production process of levulinic acid has great chances of being highly sustainable on a large scale. This inference also takes into consideration the raw material used which, in turn, does not fail to add a positive sense to the simulation in the face of new global environmental trends.

One of the great innovations of the proposed simulation is the recovery of the top stream of column B11 with subsequent separation and concentration of formic acid at elevated purity levels. In this present work the formic acid was recovered by adsorption with activated charcoal, which is a compound often used in the water treatment process, has low market value, and can be reused a few times before being discarded. Furthermore, according to the simulation data the adsorption unit operation is exothermic and releases approximately 3 kW of energy, therefore, hot utilities would not be needed at this stage of the process. The separation of formic acid is important despite its low market price, since it is used in the production of formaldehyde, rubber, plasticizers, pharmaceuticals, and textiles (Lewkowski, 2001). The main idea here is to bring a higher profit margin to the overall plant.

4. Conclusion

In this work it was evaluated the operational feasibility of a large scale levulinic acid production plant. Considering the lack of knowledge about the great potential of levulinic acid uses, one of the objectives of this work was carrying out a plant simulation to produce a 8 kiloton/year of levulinic acid. To make it possible, data from the open literature about simulations and pilot plants were used. The process seems to be viable and sustainable, generating small amounts of residues and requiring low amounts of catalyst when compared to the quantity of products generated. In addition, it is being used an inexpensive raw material.

In terms of innovation, the work brought as an alternative the recovery of formic acid which may improve the process profit margin and reduce the environmental impact in the long term. The most worrying observation about the simulation relays on the high energy demand required by the separation steps. In fact, separations of dilute aqueous solutions present this problem, future studies aiming alternatives to the presented process will be widely tested and brought in future works.

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