

# Simulation of Poly-lactic Acid Production from Sugarcane Bagasse Constituents Extracted with Supercritical Water

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Lignocellulosic materials can come from a variety of sources, including agro-industrial residues, and can serve as raw material to produce various chemical compounds. There is an appeal to produce bioplastics from lignocellulosic materials because they have similar applications and are biodegradable. For instance, the use of poly-lactic acid (PLA) has been encouraged to meet the demand for alternatives that reduce the environmental impacts caused by plastic waste. Before obtaining bioplastics, the lignocellulosic material (sugarcane bagasse) undergoes a pre-treatment process to make its constituents available (cellulose, hemicellulose, lignin and others). Thus, they can be fermented by producing microorganism. The supercritical technologies (such as H<sub>2</sub>O) in the pre-treatment and conversion of cellulose represents an alternative to conventional methods as they generate less waste. Given this scenario, this work aimed to study the production of PLA, derived from sugarcane bagasse constituents and fermentation by *Bacillus coagulans* to produce lactic acid (LA). Thus, the steps of supercritical pre-treatment, fermentation for LA production and polymerization (PLA production) in the Aspen Plus simulator were simulated. The results showed that it was possible to simulate all steps, a compatible route, being able to aggregate these processes in an ethanol production biorefinery. In this way, a strategy can be traced to conduct future simulations involving new scenarios.

## 1. Introduction

The use of plastic materials or non-biodegradable polymers has increased over the years in Brazil, a pace that recycling has not been able to keep up with. This results in a large volume of waste that accumulates, mainly, in landfills and that can generate environmental problems. The problem has worsened with the Covid-19 pandemic, studies point to a reduction in the recycling of post-consumer plastic waste in 2020, when compared to 2019 (Abiplast, 2021).

Another very positive point linked to the production of bioplastics is the use of residues of lignocellulosic materials as raw material to obtain the monomer, as seen in El-Sheshtawy et al. (2021), Derabli et al. (2022) and Yousuf et al. (2018). Cassava residue was used for LA production after enzymatic treatment by the action of microorganisms *L. rhamnosus* and *B. coagulans* (Chen et al., 2020). Rodrigues (2012) studied experimentally La production from hydrolysate obtained from steam exploded bagasse, resulting in a good productivity.

LA is an important acid because it has countless applications in several industries. Literature shows some examples of LA production process modelling, as seen Dey and Pal (2013) that developed a model and simulation of continuous LA production from sugarcane juice in membrane integrated hybrid-reactor system.

The steps leading up to the production of PLA represent a challenge on an industrial scale. Lopes et al. (2014) investigated the PLA production, aiming to reach a material for using as biomaterials in biomedical fields. The studies in this area are associated with the suitability of the process with possible scenarios that may result in higher production, minimization of environmental impacts or cost reduction, desirable characteristics, such as high molecular weight number (MWN), but PLA production is unlikely without an adequate project subsidized by simulators.

Process simulators can support prospect systems for scaling up, for example, simulate scenarios for hydrolysis, fermentation and polymerization. The feasibility of using lignocellulosic material with the release of its fractions by supercritical fluids can be investigated using simulators. A proof of this is the use of simulators for all these phases, as has been reported in Farias-Campomanes et al. (2013), Albarelli et al. (2018) and Pérez-Cisneros et al. (2015), but they are still scarce.

The simulation of the LA production stage also reveals some barriers that still need to be studied, such as pH control during fermentation processing. Méndez-Alva et al. (2018) reported the implementation of a processing platform aided by simulations and analysis of a possible route for the industrial production of AL from sugar industry residues.

The aims of this study are to reveal simulations using ASPEN Plus tools of the three steps: obtaining lignocellulosic fraction (from sugarcane bagasse) using supercritical water; fermentation of the lignocellulosic fraction to obtain LA; and polymerization of LA. To present the importance of connecting the different areas, such as engineering, chemistry and biotechnology, in order to achieve sustainable production and lead to important biorefinery related projects.

## 2. Methodology

A flowsheet of the system was developed using Aspen Plus v10.1. The streams are divided into liquids and solids and its representation, properly, it was used MIXCISLD steam class in simulator. The most chemical compounds used in this process were available in simulator database, such as water (H<sub>2</sub>O), but some needed to be specified, such as Cellulose ([C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>]<sub>n</sub>) and hemicellulose ([C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>]<sub>n</sub>). Many steps can be considered for lignocellulosic material under critical conditions to promote hydrolysis (Albarelli et al., 2013). There are many different mass composition (%) of sugarcane bagasse from the several sources, so it was considered for this study according to Silva et al. (2011), Table 1:

Table 1: Chemical composition of raw sugarcane bagasse

Composition	Raw sugarcane bagasse (%)
Cellulose	42.8
Hemicellulose	25.9
Lignin	22.1
Ashes	3.1
Moisture	6.1

It was considered conversion the lignocellulosic fraction into glucose and xylose, because of homofermentative considerations.

### 2.1 Hydrolysis of lignocellulosic material in supercritical water

The strategy proposed was to work with two reactors based on Zhao et al. (2011). For simulation, the sugarcane bagasse and water were pressurized up to the reactor pressure, thus the cellulose was dissolved and hydrolyzed in the first reactor. Main parameters used for simulation (this stage) were: operating temperature 380 °C; operating pressure 220 bar; residence time 10 s, cellulose/glucose conversion 95% and hemicellulose/xylose conversion 95%. The mixture was cooled and taken to the second reactor to convert (from hydrolysis) oligosaccharides into hexoses. The parameters used were: operating temperature 240 °C; operating pressure 90 bar; residence time 50 s. The product was washed for the release of the total sugar and concentrated up in a multi-effect evaporation system before being sent to fermentation. These stages were summarized in Figure 1.

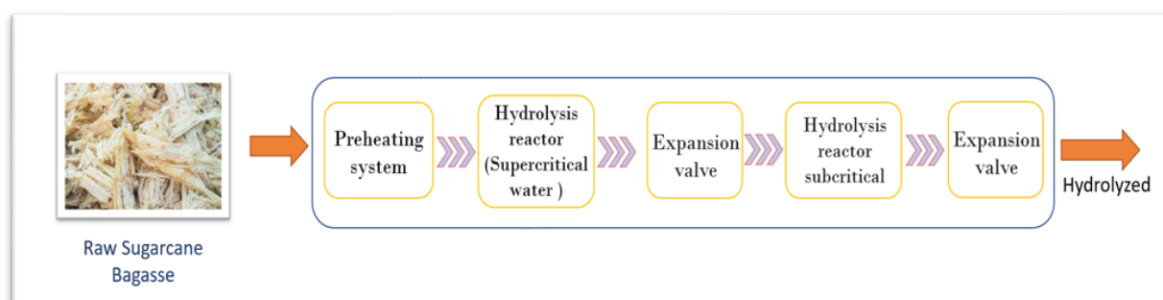


Figure 1: First stage – hydrolysis supercritical water.

## 2.2 Fermentation of lignocellulosic fraction

This stage represents the conversion of glucose and xylose (from hydrolyses) in LA. The microorganism considered was *Bacillus coagulans* because its production of LA (including L-isomers) is widely reported in the literature, such as Oliveira et al. (2019). For development of the simulation, it was needed to identify the main reactions on Aspen Plus. Some information are missing related to conversion parameters, so they were not considered in system.

The fermenter was represented by stoichiometric reactor operating in ambient pressure and temperature controlled. The foot tub had 30 % in volume and the glucose and xylose conversion considered was 100% according to Rodrigues (2012). These stages were summarized in Figure 2.

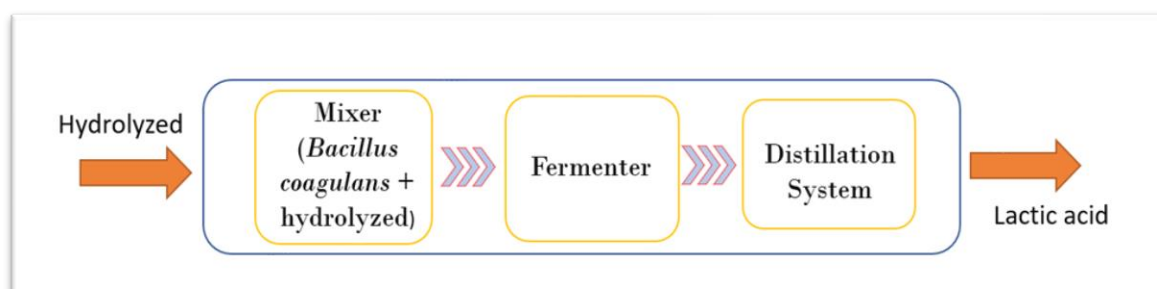


Figure 2: Second stage – Sugarcane bagasse hydrolyzed in Fermenter.

## 2.3 LA Polymerization

The process of LA polymerization was based on Martinez et al. (2011) and some points on Savioli et al. (2014). The system was divided in three stages for oligomers, lactide and poly-lactic acid (PLA) formation. First, the solution from the fermenter followed to oligomerization reactor where it was removed the water. The product was conducted to CSTR reactor and a distillation column to recycled lactic acid. It was used a stannous catalyst for dimer formation. This outflow was connected into a purification system (flash evaporator and distillation column), in order to separate the dimmer of the other products. There was a recycle for LA and water conducting to the oligomer formation stage. The lactide was polymerized to polylactide, resulting a mixture which was passed on to a multistage evaporation. Two separator blocks were utilized to discard the catalyst (considering the catalyst neutralization) and to achieve the purified PLA. These stages were summarized in Figure 3.

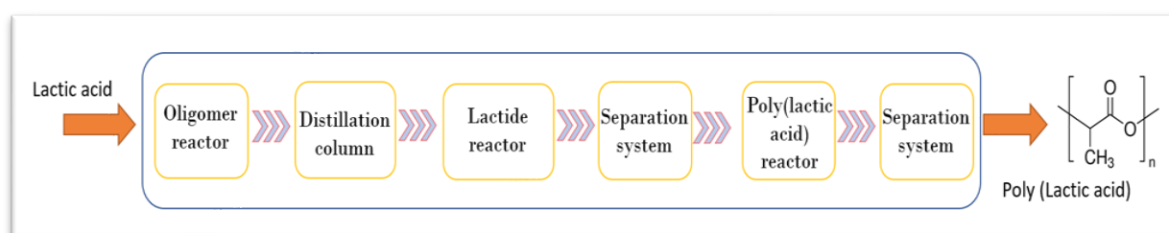


Figure 3: Third stage – Sugarcane bagasse hydrolyzed in Fermenter.

The objective of the Oligomerization process was to reach PLA oligomers of low molecular weight without catalyst. To achieve the highest mass flow of PLA, the reactor must be performed at vapor-liquid phase, temperature 201 °C, pressure 2 atm, residence time 4 hr.

## 3. Results

### 3.1 Evaluation of biomass hydrolysis

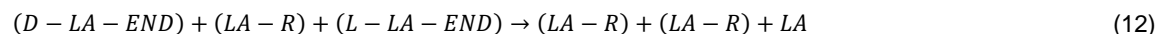
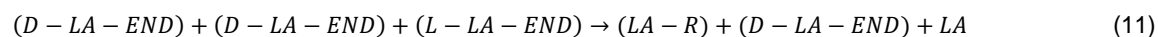
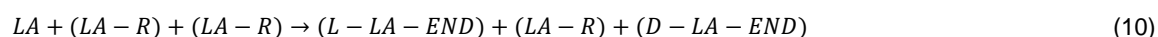
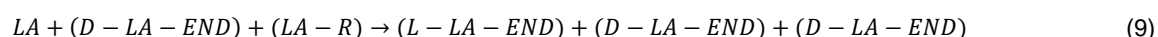
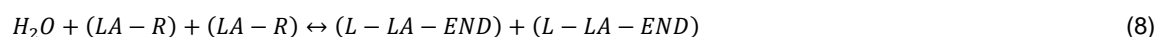
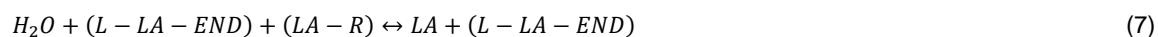
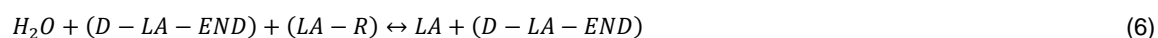
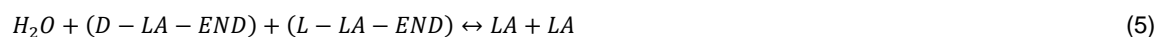
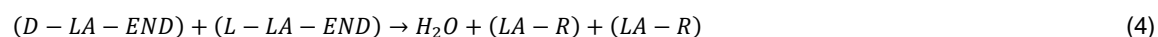
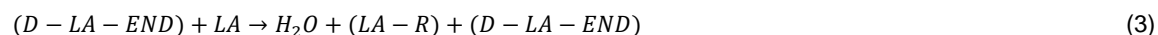
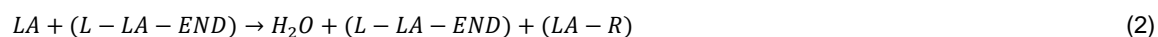
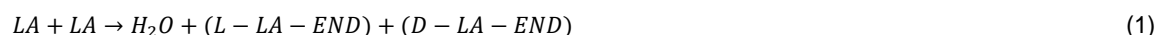
The bagasse stream pumped was heated to 100 °C at a heat exchanger and sent to the hydrolysis reactor. The supercritical water inlet in the reactor is defined by the amount of water necessary to heat the biomass to the desired reactor temperature. The simulation showed that energetic consumption is high, requiring an extra heat source. Other scenarios should be studied to enable, such as to simulate several processes together.

### 3.2 Fermentation system

The fermentation process by *Bacillus coagulans* has active metabolic pathway from glucose and xylose in homofermentative way. Therefore, biomass hydrolysis using supercritical water to release the compounds can represent an interesting route when referring to industrial processes. It is important to highlight that this microorganism has high yield and productivity (100% conversion), moreover, without ethanol and acetic acid production (can be inhibitors). The temperature 52 °C was acceptable for all sugar source conversion into lactic acid, using pressure 1 atm.

### 3.3 Polymerization System

In the development of this simulation, the model used was *step-growth* to represent the polymerization, the package is available for several reactions. It This model generated a series of reactions based on functional groups. Thus, it was necessary to define the structures of the reactants in terms of nucleophilic and electrophilic, then the reactions were generated (Eq 1-12), assessing the possible routes in which the species can react.



\* $(L - LA - END)$ -terminal segment L of lactic acid;  $(D - LA - END)$ - terminal segment D of lactic acid;  $(LA - R)$ -repetitive segment of lactic acid.

This model showed direct (Eq 1-4 and 9-12) and reversible (Eq 5-8) reactions, as well as subsequent rearrangement reactions. This was possible because the reaction model uses database from types of segments to determine how polymerization reactions influence the properties of polymers such as degree of polymerization and Molecular Weight Number (MWN). It is important to emphasize that the nature of the models employed is stochastic and some kinetic parameters were implemented based on Seavey e Liu (2008). Other point, whether the LA concentration is very low, the reaction will be completed slowly and the MWN of PLA will be very high. Thus, whether the LA concentration and water amount are very high, it would be impossible to achieve a high PLA MWN.

Taking this information into account, it was used a stannous catalyst for obtaining PLA with high MWN. Table 2 presents the main results of LA, lactide, water, PLA streams and MWN in each stage.

Table 2: The main results of variables in PLA production

Variables	Oligomer reactor	Lactide reactor	PLA reactor
LA (g)	337.35 kg/h	572.61 kg/h	30.74 kg/h
Lactide (kg/h)	0.0 kg/h	11,761.01 kg/h	1,596.11 kg/h
Water (kg/h)	194.22 kg/h	515.87 kg/h	0.50 kg/h
PLA (kg/h)	10,086.17 kg/h	97,228.58 kg/h	9,882.51 kg/h
MWN	623.55	949.75	53,417.54

\*Corresponding values liquid phase

The results of this system showed that it is possible to produce high PLA MWN. To obtain PLA with the desired characteristics, firstly, it was necessary to produce low PLA MWN and then lactide.

This study clarified which directions new simulations should take from experimental data, establishing a path that still needs to be deepened for the real implementation of a biorefinery. It is important to emphasize that this study has a preliminary character based on some simulation and experimental works, more analyses must be done in new stages.

#### 4. Conclusions

Simulations in commercial software (ASPEN Plus) of the production of PLA from the fermentation of La hydrolysate from sugarcane bagasse were verified to enable some stages of the biorefinery, mainly in conjunction with the production of ethanol. In the literature, there is no record of works dealing with the production of PLA from bagasse with supercritical treatment. Treatment of sugarcane bagasse with water under critical conditions (hydrolysis) was able to show that more research is needed in terms of evaluating other compounds such as arabinose formation and then directions of the separation process, for example membrane. It, also, was assessed the potential for homofermentative LA production from hydrolysed as substrates, which contain a mixture of sugars (glycose and xylose). Other simulations considering the acetic acid and ethanol production in fermenter, heterofermentative route, have an economic impact on the separation process. According to the results of LA polymerization, high value of PLA MWN (53,417.54) can be achieved, attracting interest for large-scale production due to the various applications of the polymer.

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