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Computational Implementation of Required Industrial Unit Operations for Bio-Plastic Production From Starch Extracted from Banana Peels by Aerobic Fermentation using *Rizophus Oryzae*

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Abstract. In this research computer modeling was performed with the SuperPro Designer Software to simulate the industrial-scale production of poly-lactic acid using the *Rizophus oryzae* fungus. The previous to predict the higher output of poly-lactic acid from different strategies: in the first study, a PLA production of 5.56 (kg/h) was obtained with an operating cost of USD 121,722,644/year. Based on the results, improvements were made to the process. The first alternative resulted in a PLA production of 43.64 (kg/h) with a total operating cost of USD 37,356,085/year. The second improved significant differences in terms of the most massive production of PLA was 64.97 (kg/h), with an annual operating cost of USD 55,334,811 being the most promising to be carried on an industrial scale.

1. Introduction

Banana (*Musa spp.*) is one of the essential fruits in developed countries from Asia, Latin America and Africa. In Colombia, the departments of Quindío, Meta, Antioquia, Tolima, Caldas, Córdoba, Risaralda, Valle, Nariño and Cauca, are the largest banana producers. These regions representing 80% of the production and 65% of the area planted in the country, which for the year 2013 was 394.351 hectares and a production of 3.351.983 tons of which 3.8% is exported; About 1% is used for the consumption of agribusiness and losses equivalent to 10% of production are estimated. The rest is consumed in rural and urban households in the country [1]. The banana peel represents 35% to 40% of the fruit. The latter is an organic waste that can be used to manufacture different value-added products, including starch extraction, which has numerous applications in the paper industry, textile, pharmaceutical (as excipient), adhesives, food (as a thickener), water treatment (coagulant) and polymers [2]. The use of fungi has advantages because of the amylolytic characteristics and low nutrient requirements. The morphology of mushrooms is an attractive characteristic in acid production because it can influence positively as well as negatively.

Fungi can grow can growth forming a granular mycelium, flocs and spherical pellets. This latter form exhibits a higher lactic acid yield than a flocculate form. Fungal fermentation has the advantage of requiring a simple culture media to produce lactic acid but also has high aeration requirements [3]. *Rhizopus oryzae* fungus has been studied for the biotechnological production of lactic acid since it has the advantage that it does not require an organic nitrogen source for its growth. Also, it can directly produce large amounts of L (+) lactic acid and is easily separated from the fermentation medium in recovery and purification process. Research has recently been accelerated in L (+) and D (-) lactic acid by biotechnology due to its possibility of transformation into biodegradable polylactide (PLA) [4]. Currently, the use of waste as a raw material in biotechnological processes is emerging as an attractive

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alternative to reduce oil dependence. The latter because polypropylene and polystyrene are commonly obtained and new products such as bioplastics could also be produced. One of the most advantages of this technology is its perseveration of non-renewable energy sources such as oil [5]. The use of bioplastic materials is spreading in several sectors: in medicine (prostheses, sutures), in food (catering products, disposable containers), toys, and even in the world of fashion and, for course, in biodegradable bags.

Bioplastic disposable products degrade in less than one year. Plastic and expanded polystyrene disposable products that can take up to 1200 years to degrade, generating cumulative pollution to the ecosystem [6]. Due to the limitations presented by natural polymers as raw materials for the production of bioplastics, today, the most significant development focuses on the bioplastics obtained by microbial fermentation. The cross-linking of PLA chains results in a biodegradable plastic that serves as the basis for the production of numerous non-polluting plastic products. The products obtained can be injected, extruded and thermoformed as healthy as conventional petroleum-derived plastics and have the same physicochemical properties. PLAs are flexible, easily mouldable, resistant and with a sound moisture barrier [7]. Polymerization of lactic acid results in polylactic acid: a biopolymer that possesses D- and L-isomers or a racemic mixture of this thermoplastic. PLA can be prepared by different polymerization processes from lactic acid, including polycondensation, ring-opening polymerization and direct methods such as azeotropic dehydration and enzymatic polymerization. Direct polymerization and ring-opening polymerization are the most used production techniques. Condensation polymerization is the least expensive PLA synthesis route.

On the other hand, ring-opening polymerization (ROP) is the most common route to achieve high molecular weight. This route requires additional stages of purification that is relatively complicated and expensive [8]. However, the feasibility of obtaining PLA is currently questioned since, according to the authors' knowledge, there are no reports of bioproduct costs on an industrial scale to define its technical-economic feasibility from the banana peel. Based on the preceding, computational simulation can be a potential tool to predict the production of PLA on an industrial scale. So that, through mass and energy balances numerical processing, it is possible to determine not only the requirements of materials and energy required but also the economic-technical pre-feasibility of a bioprocess. That is why, in this research, computational modelling was performed with the SuperPro Designer Software to simulate the production of PLA (polylactic acid) using the *Rizophus oryzae* fungus on a large scale. The above with the primary objective of predicting the higher poly-lactic acid production from different production strategies.

2. Methodology

The industrial-scale production of PLA can be achieved through the implementation of Upstream and Downstream stages, as shown in Figure 1.

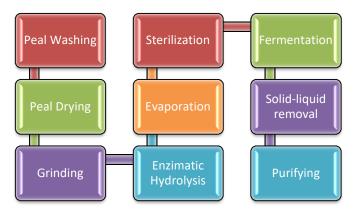


Figure 1. Upstream and downstream implementation for large scale PLA production.

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The first stage consists of unit operation design for culture media preparation (Washing of the material, Drying, Grinding and Hydrolysis), sterilization, inoculum production. During the Downstream, the final product is separated and purified until the PLA is obtained.

2.1 Description of Upstream Stages

The banana peel is composed of Starch, Cellulose, Hemicellulose and Lignin and its composition is defined in Table 1 [9].

 Component
 Value

 Starch
 39.89

 Celullose
 13.20

 Hemi-cellulose
 14.80

 Lignin
 14.00

 Solid residuals
 5.00

 Water
 13.10

Table 1. Banana peel composition for culture media preparation.

However, it is processed to convert the starch into a simpler carbon source to be metabolized by the microorganism. Therefore, the unit operations required at this stage are material washing, drying, grinding and hydrolysis. Enzymatic hydrolysis is proposed to add a pool of enzymes (β -glucosidases, Endo- β -1, 4 glucanases and Exo-1,4-glucanases) to convert the starch into monomers such as glucose, by the enzymatic route. Once the sterile fermentation media is obtained, the latter is pumped to production tanks. At this stage, glucose to lactic acid conversion process is carried out by the following generalized biochemical reaction in equation (1):

$$Glucose + Oxygen + Salts \rightarrow Biomass + CO_2 + Lactic Acid + H_2O$$
 (1)

The fungi used in the lactic acid production are molds and yeasts that belong to the genera *Rhizopus, Zymomonas, Saccharomyces and Kluiveromyces. Rhizopus oryzae* has been widely used for biotechnological lactic acid production since it has the advantage that it does not require an organic nitrogen source for growth. Also, it can directly produce large amounts of L (+) lactic acid and is easily separated from the fermentation medium during the recovery and purification process.

However, its physical form hinders lactic acid production since the large size of the mycelia can cause an increase in the media viscosity, which creates a high resistance to mass oxygen transfer in the fermentation process [10]. The latter increases fermentation times and also by-products formed, especially ethanol and undesired metabolites, are increased.

In this Research, a glucose concentration of 190 g/L at the bioreactor inlet is proposed to achieve a biomass yield to the substrate of 0.11 g/g and a lactic acid yield of 0.87 g/g [4]. A production volume of 1000 liters is proposed.

2.2 Description of the Downstream Stages

The biomass and solid particles are separated from the fermentation medium using a centrifuge. Then the lactic acid obtained is purified. Initially, a distiller is used to separate the ethanol. Then filtration equipment to recover the remaining biomass and enzymes is used. The above, to remove residues from the culture medium. Chromatography was performed to separate components of the desired product. Acetic acid, sodium chloride and WFI (high purity water) are added and finally, a diafiltration is used sodium chloride removal. Polylactic acid (PLA) is a thermoplastic biopolymer converted from the lactic acid precursor. Due to its biodegradability, barrier properties and biocompatibility, PLA has found numerous applications, from the amorphous state to the crystalline state. This latter can be achieved by manipulating the mixtures between the D (-) and L (+) isomers, molecular weights and copolymerization. Once PLA is obtained in the solid-state, this latter is lyophilized to make it more convenient for transport. Lyophilisation consisted of freezing the material and then reducing its

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surrounding pressure to allow the frozen water in the material to sublime directly from the solid phase to the gas phase without going through the liquid state. For the lactic acid polymerization process into polylactic acid (PLA), a chemical reactor is used. Next, the reaction occurs there in equations (2) and (3):

$$Lactic\ acid\ \to\ Lactide\ +\ H_2O \tag{2}$$

$$Lactide + Octoate\ tin \rightarrow PLA$$
 (3)

3. Results and Discussions

Petroleum-derived plastics (petrochemicals) are non-degradable and highly waste for the environment. Currently, these products are being replaced by the manufacture of bioplastics for its extraordinary properties. The PLA, composed of various natural polymers, provides better characteristics such as water resistance. This bioplastic is the best option for packaging to reduce the waste generated by the usual packaging. The main advantage of the production of PLA bioplastic in the simulation performed using the Rizophus oryzae is that fermentative production uses products derived from agriculture as a carbon source. So that in this research, an industrial scale bioprocess was designed to transform an agro-industrial waste from banana peels to obtain PLA. The findings found here also suggest that byproducts derived from PLA production can be obtained, such as ethanol that could be marketed or used as an energy source for the same PLA production plant. Another advantage is that it has flexibility characteristics, efficiently moldable, resistant and suitable moisture barrier capacity. All of these are depending on the production process. The PLA produced has an excellent odor barrier, high transparency and brightness. That is why its application in medical packages and fibbers can be of great interest in medical applications. According to the results obtained in this research, it is possible to get a PLA production of up to 5.56 (Kg/h) with a total operating cost of 121,722,644 (USD). The standard diagram of the simulated process using the SuperPro Designer computational tool is illustrated in Figure 2 and its nomenclature is presented in Table 2.

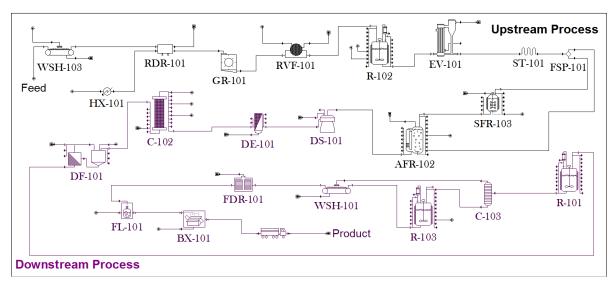


Figure 2. Large scale bioprocess proposed for PLA production using SuperPro Designer (Standard).

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Table 2. Nomenclature Defined for large scale PLA unit operations

Name	Unit Operation
WSH	Washing
HX	Heating
RDR	Rotary Drying
GR	Grinding
RVF	Rotary Vacuum Filtration
R	Reactor
EV	Evaporation
ST	Heat Sterilization
SFR	Seed Fermentation
AFR	Air Lift Fermentation
DS	Centrifugation
DE	Dead-End Filtration
C	Chromatography
DF	DiaFiltration
FDR	Freeze Drying
FL	Filling
BX	Packaging

The total annual production costs are discriminated according to raw material, energy required for the operation of industrial equipment, personnel and consumables (filtration membranes, chromatography resins, etc.) costs. In Figure 3, it is observed that industrial equipment consumables represent 80 % of the total costs. The above, due to the chromatography stages proposed to separate and purify components. This interesting finding allows offering strategies to reduce operating costs during obtaining PLA through biotechnology. That is why the first strategy aimed in this research to reduce costs is to replace the chromatography column with a distillation tower, based on the difference in boiling points of lactic acid, with a value of 122 ° C [11] and depleted culture medium, mostly composed of water (100 ° C). It should be mentioned that lactic acid is the precursor for the generation of PLA by a polymerization process previously described.

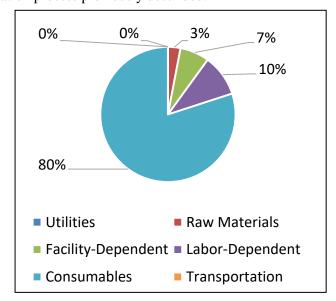


Figure 3. Operating costs for large scale PLA production(Standard).

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Distillation is a unit operation that allows components to be separated using their volatility, so that water is removed at this separation stage. According to results, this alternative resulted in a PLA production of 43.64 (kg/h) with a total operating cost of USD 37,356,085/year. That is why the unit cost of the product went from being 2.76 USD/g to 0.10 USD/g. The latter indicates an operating costs reduction by more than 90% (see Figure. 6). The PLA production on an industrial scale using the strategy above to reduce costs is shown in Figure 4 (see Table 2 for nomenclature definitions).

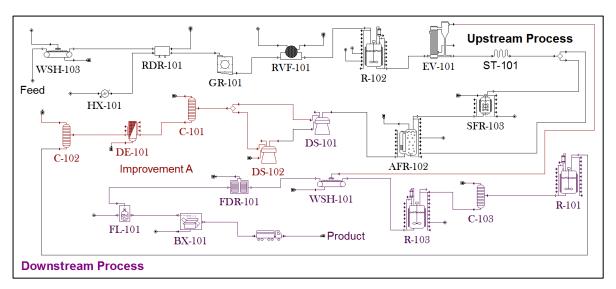


Figure 4. Strategy A for large scale PLA production.

Many microorganisms synthesize bioplastics. For industrial manufacturing, microorganisms are required to be able to ferment economic substrates wholly and quickly, minimizing nutrients, and the amount of biomass and resulting by-products. There are a variety of raw materials that can be used.

These must fit specific parameters such as low cost, low pollutant index, high lactic acid productivity and easy access to these as was the case of the banana peel used in this process. This latter is a food of high commercial demand. Also, it generates a large amount of waste and can be an alternative to the environmental problem. The improvement strategy B consists of production plant under the concept of multi-products implementation [12]. This strategy includes the use of other byproducts obtained simultaneously during the production of lactic acid using the same industrial machinery. That is why *Rizophus oryzae* fungus also generates ethanol during the fermentation process. The latter metabolite is widely known not only in the fuel alcohol industry but also in pharmaceutical and medicinal applications. Ethanol can also be recovered by a distillation operation, so that the ethanol is removed in this second stage of separation, achieving an 80% recovery of ethanol, according to the results obtained in this work (see Figure 5 and Table 2). That is why using the concept of multi-products, this plant could generate competitive profitability. According to the results, these products can be obtained simultaneously with lactic acid production with an estimate of 21.33 kg/h of ethanol. Therefore, global production is increased until a value of 64.97 (kg/h) with an annual operating cost of 55,334,811 USD being the most promising to be taken on an industrial scale.

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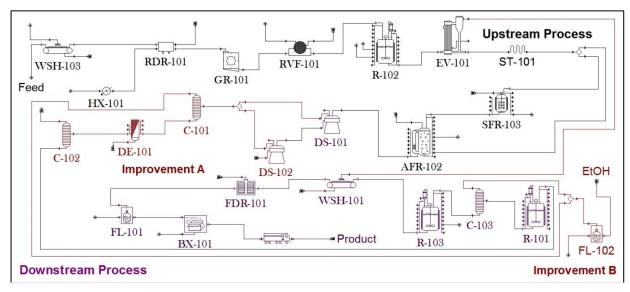


Figure 5. Strategy B for large scale PLA production.

Considering the above, ethanol production would comprise 30% of the global multi-product productivity obtained in this industrial plant, while the remaining 70% would correspond to the production of lactic acid. The PLA operating costs would also represent 70% of the overall cost. According to the results, the total cost in strategy B results in 0.1075 USD/g, indicating that the PLA unit operating cost would be estimated at 0.072 USD/g. The above shows a 30% reduction concerning strategy A, significantly impacting the cost reduction associated with required personnel and equipment use (see Figures 6-7) cost. Based on the results obtained in this work, computational simulation can be a potential tool to predict PLA production on an industrial scale. So that, through numerical processing, it is possible to determine not only the materials and energy requirements but also the bioprocess economic, technical pre-feasibility. According to the results, PLA industrial-scale production can be a promising process for the pharmaceutical, medicinal and environmental industries. The latter considering its possibilities for obtaining a product with an added value from renewable sources other than petroleum and also, at the same time, it uses environmentally friendly technologies.

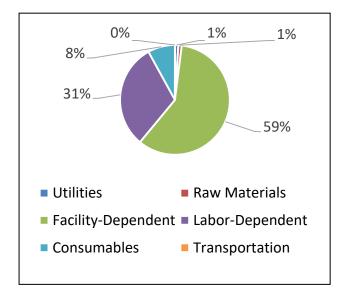


Figure 6. Operating cost estimations for large scale PLA production (Strategy A).

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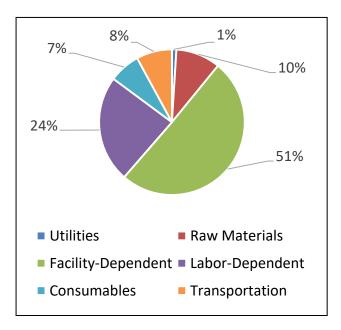


Figure 7. Operating cost estimations for large scale PLA production (Strategy B).

4. Conclusions

The PLA purification using Chromatography on an industrial scale can represent up to 80% of the operating costs due to consumables requirements like resins. Therefore, it can be a costly stage to be implemented at the industrial level. The distillation operation on an industrial scale as an alternative to Chromatography. It can reduce the PLA unit operating cost on an industrial scale by more than 90% using biotechnology. The PLA unit operating cost, according to is estimated at 0.072 USD/g to the results calculated in this research.

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