Analysis of the ethanol and butanol production at different scales from plantain peel and Eucalyptus globulus

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Abstract: Currently the use of biofuels is a subject of great interest due to the pollution generated by the use of fossil fuels. Biofuels are generated by fermentation from agro-industrial waste generating a greater positive impact on the environment; these must have a pretreatment to obtain the fermentable sugars. Ethanol is undoubtedly the most studied compound as an alternative to traditional fuels, however, in the last decades butanol has begun to be evaluated for its great advantages that it presents on ethanol. In this paper, plantain peel for small-scale and Eucalyptus globulus for high-scale are evaluated as raw materials in the stand-alone ethanol and butanol production processes. For the plantain peel an acid pretreatment followed by an enzymatic hydrolysis is evaluated and for the Eucalyptus globulus an autohydrolysis before the enzymatic hydrolysis. As a result, it was demonstrated that the ethanol production is a more cost-effective process than the production of butanol. However, butanol has greater advantages over ethanol as a fuel because of its energy content. In the high-scale processes, the costs of using the utilities decrease because better energy integration can be made to take advantage of the process streams.

Keywords: Biofuels, Ethanol, Butanol, Plantain peel, Eucalyptus globulus

1. Introduction

Currently, fossil fuels represent 80% of the energy consumed worldwide [1]. Sources of production of these fuels are depleted over time. The use of these fuels produces problems such as greenhouse gases, melting glaciers, destruction of ecosystems, etc [1]. The increasing of energy demand leads to an increase in crude oil prices directly affected by the global economic activity [2]. Additionally, the availability of crude oil is becoming less, as in the world it is found a new barrel of oil for every four that are consumed [3]. All these factors have driven the search of new or better alternatives to oil and the biomass as renewable feedstock appears as a good option. The biomass is renewable, abundant, available and low cost. It can be converted into renewable energy by different technological processes such as combustion, alcoholic fermentation and gasification, among others [4], [5]. The use of biomass as a raw material presents advantages like decrease in process costs, reduction of wastes and decrease of hazardous emissions, reducing the impact generated in the environment [6], [7]. The production of biofuels is a great alternative to replace fossil fuels. Biofuels as for example bioethanol, methanol, biobutanol, biodiesel, Fischer-Tropsch diesel, hydrogen and methane are produced from biomass [8]. Of all biofuels mentioned above, ethanol has been the most studied [9]–[12].

As biofuel, the ethanol can be used as a gasoline additive to increase the oxygen content and consequently to reduce the emissions to the environment. Instead, in the last years different studies have been carried out to find biofuels with the same or better characteristics than ethanol. During the researches butanol has generated great interest due to the characteristics as biofuel. Butanol has many advantages over ethanol. The main one is the largest number of carbons providing to butanol most energy content than ethanol. Other advantages characteristics as less corrosive, less volatile, better blending ability and lower vapor pressure, among others [13], [14]. In summary, for the same volume of gasoline the butanol achieves the 95% of energy, while the
ethanol only the 75% [15]. The butanol can be mixed with conventional gasoline in a high proportion without having to adjust the car engines[16]. It tolerates better water contamination with less corrosion problems [17].

Both components can be produced by fermentative and petrochemical via. However, the production by fermentation is the route most interesting, since it allows the use of waste as a raw material, making the process less polluting than the petrochemical process. Additionally, the last is dependent on the oil, which makes that the variations in its value influence in the economic stability of the process. The sugars required for the fermentation can be obtained from the agro-industrial residues through a pretreatment stage. The use of these residues to obtain fermentable sugars has been studied and have proven to be effective [18]–[20]. Residues as sugarcane bagasse [9], coffee cut stems [21], rice straw [22] and corn stover [23] have been used to produce ethanol and butanol. These residues are good candidate for substrates in the production of biofuels. Its use give an added value to the process because it generates benefits on the environment by reducing the pollution generated and has not competition with the food industry [15].

_Eucalyptus globulus_ is used to obtain pulp, fiberboards, lumber and furniture, among others [24]. From these processes, a residue is obtained that is lignocellulosic biomass of wood origin with high contents of cellulose and hemicellulose that allow obtaining fermentable sugars [25], [26]. Extension of crops and the big use of _Eucalyptus globulus_ in the industry makes the amount of waste generated large enough for use in large-scale biorefineries. The increase in the use of plantains in the food industry has led to an increase in the amount of waste generated [27]. The plantain peel represents 40% of the total weight of the fresh fruit and the accumulation of these seeks to give them use without causing environmental contamination [28]. The plantain peel has a high lignin content but the hemicellulose concentration is low [29]. However, it is possible to obtain high concentrations of sugar due to the amount of soluble sugars [29]. Peel residues generated in plantain crops are smaller compared to other crops such as eucalyptus, so they can be used in low-scale biorefineries.

Based on this, _Eucalyptus globulus_ and plantain peel are chosen as raw materials for the development of this work. Initially the physicochemical characterization of each of the raw materials is carried out following accepted international standards. Subsequently for the eucalyptus globulus, a pretreatment stage of autohydrolysis followed by enzymatic hydrolysis is evaluated experimentally. For the plantain peel this stage consists of a dilution acid treatment followed by an enzymatic hydrolysis. Then four scenarios are proposed for the stand-alone processes of butanol and ethanol from each of the raw materials, taking into account that the eucalyptus globulus is for high scale and the banana peel for low scale. Finally, these scenarios are evaluated technically and economically with Aspen Plus software.

2. **Methodology**

For the development of this work, a methodology is proposed. That starts with the experimental part, composed by the characterization of the _Eucalyptus globulus_ and the plantain peel, and by the evaluation of the respective pretreatments. Then with the obtained data a simulation was done to evaluate technically and economic the proposed schemes.

2.1 **Raw material characterization**

The raw materials were chemically characterized following internationally accepted standards. Moisture was determined with AOAC 925.09 standard [30], ash with the NREL/TP-510-42622 standard [31], extractives with NREL/TP-510-42619 [32]. The cellulose, the lignin and the total carbohydrates in the plantain peel was determined with T 203 os-74 [33], T 222 os-74 [33] and sulfuric acid-phenol method [34], respectively. The structural carbohydrates and lignin in the eucalyptus was determined with NREL/TP-510-42618 method [35].

2.2 **Pretreatments**
An acid pretreatment followed by an enzymatic hydrolysis is evaluated to obtain the sugars from the plantain peel and an auto-hydrolysis is assessed to obtain sugars from the Eucalyptus globulus. The concentrations of sugars for all the pretreatments were determined by HPLC.

2.2.1 Acid pretreatment

Before the pretreatments the plantain peel was dried at 50 °C until it has less than 10% humidity and then milled and sieve to obtain a particle size of 0.42 mm (40 mesh), approximately. The acids decompose the cellulose and hemicellulose found in lignocellulosic biomass to sugar molecules. The conditions for this pretreatment were acid concentration 2% (v/v), temperature 115 °C and pressure 15 psia. The solid to liquid ratio was 1:10 (w/w) and the reaction time 1 hour. After the pretreatment, the solid portion was washed with hot water until the pH neutralization.

2.2.2 Autohydrolysis

This process was developed according by [36]. In the autohydrolysis a solid to liquid ratio of 1:6 was used, the solid was Eucalyptus globulus wood chips and the liquid only distilled water. This mixture was held for 12 h to allow the water impregnation, and then it was kept at 175 °C and 125 rpm during 43 min.

2.2.3 Enzymatic hydrolysis

This process usually goes after the acid pretreatment and the autohydrolysis because is slow and affect economically the process. The enzymatic hydrolysis was developed following the NREL/TP-510-42629 “Enzymatic Saccharification of Lignocellulosic Biomass” [37] using a solid to liquid ratio to 1:15 (w/w) at 50 °C and 150 rpm.

2.3 Simulation

Before the experimental characterization and the pretreatments each process was simulated whit the software Aspen Plus (Aspen Technology Inc., USA) commercial package, this tool generated mass balances and energy balances to made an integral analysis of the process, that allows knowing the technical viability. Based on the components present in both process the thermodynamic model used is the Non-Random Two-Liquid (NRTL) to calculate the activity coefficients of the liquid phase and the equation of state of Redlich-Kwong for the modeling of the vapor phase. For the plantain peel was used a feed of 10 ton/h and for the E. globulus 1000 ton/h.

2.3.1 Ethanol production

The ethanol production was simulated with the kinetic model reported by [38], using Zymomonas mobilis as microorganism. The process start when the sugars obtained in the respective pretreatment are fed to a reactor at 30 °C whit the microorganism. Finished the fermentation, the broth enter in a separation stage at one bar of pressure. First, pass through distillation column to obtain a composition of 60% w/w, and then the stream is purified in a rectification column up to the azeotropic composition (~95%). Finally, in a molecular sieve with pore size of 4 Å the ethanol is obtained at 99.6% w/w. Figure 1 presents the flowsheet of the process.
2.3.2 Butanol production

Butanol is produced through ABE (Acetone, Butanol, Ethanol) fermentation using the microorganism *Clostridium acetobutylicum*, for the simulation the stoichiometry equations reported by [39] was used. The sugars enter to a fermenter to execute the fermentation at 37°C. After this bioreactor, the produced gases are purged. Then, the stream enters to a first distillation tower when the acetone is separated. The stream with the water and the alcohols get into a decanter to create two phases. The organic phase enters to a second distillation tower where the ethanol is separated. In the third distillation tower the butanol is purifies at 99.8%. The separation stage occurs at one bar. Figure 2 presents the flowsheet of the process.

2.4 Economic assessment

The estimation of total production costs was calculated using the Aspen Process Economic Analyzer (Aspen Technology Inc., USA) commercial software based on the material and energy balances from simulation. The production costs are estimated for ten years of service life plant using a linear depreciation method for calculating the capital depreciation. It based on colombian conditions with income tax of 33% and an interest rate of 16.02%. The cost for the plantain peel and the eucalyptus globulus was estimated in 10 USD/ton and 20 USD/ton, respectively.

3. Results and discussion

3.1 Raw material characterization

The characterization for the plantain peel and the Eucalyptus globulus are shown in the table 1. It can be seen that both raw materials have a high moisture content. This can be generate an additional energy requirement for drying. Eucalyptus globulus is a promising raw material to obtain sugars due its high cellulose and hemicellulose content. Plantain peel has large amount of extractives and low content of cellulose and hemicellulose. However, in its composition there are soluble sugars that make it a potential raw material.
Table 1. Raw materials characterization

<table>
<thead>
<tr>
<th></th>
<th>Eucalyptus globulus</th>
<th>Plantain peel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work (%)</td>
<td>Literature</td>
</tr>
<tr>
<td>Moisture</td>
<td>60</td>
<td>--</td>
</tr>
<tr>
<td>Extractives*</td>
<td>3.6</td>
<td>2.9a</td>
</tr>
<tr>
<td>Cellulose*</td>
<td>51.9</td>
<td>53.7a</td>
</tr>
<tr>
<td>Hemicellulose*</td>
<td>18.7</td>
<td>12.2b</td>
</tr>
<tr>
<td>Lignin*</td>
<td>25.4</td>
<td>20.2a</td>
</tr>
<tr>
<td>Ash*</td>
<td>0.4</td>
<td>0.38a</td>
</tr>
</tbody>
</table>

* Dry basis

Some authors report the characterization of each raw material. In the case of the Eucalyptus globulus the values obtained in this work are very close to the reported, the hemicellulose and the lignin are the components that represent great difference. For the plantain peel the extractives composition are very different. This can be influenced by the maturation grade of the plantain peel. The other components present similar values. Additionally for the plantain peel the total carbohydrates were determined to have an estimated value of the soluble sugars. Of around 40% of the plantain peel is total carbohydrates. This can influence the results in the pretreatments.

3.2 Pretreatments

3.2.1 Acid pretreatment and enzymatic hydrolysis

After the acid pretreatment, the solid and the liquid fraction were separated. The liquid had a composition of 9 g/L of glucose. Due to the acid and the high temperature some inhibitors compounds were formed in the process, the main are furfural (0.1 g/L) and hydroxymethyl furfural (2.47 g/L). The concentration of this inhibitor components depend on the acid concentration, pretreatment time and temperature. When these parameters increase the inhibitors concentration are higher [43]. Then with the solid fraction an enzymatic hydrolysis was carried out, and at the end, the fractions were separated again. The liquid fraction had 8 g/L of the glucose. That is a low value. For other components with higher content of cellulose and hemicellulose there are reported some values of glucose after an enzymatic hydrolysis: sugarcane bagasse 33 g/L [44], corn stover 17 g/L [45]. The low glucose concentration occurs mainly as result of two factors. First the cellulose concentration in the lignocellulose matrix is low, thus it does not possible to obtain high amounts of sugars. The other reason is the concentration of sugars in the liquid fraction in the acid pretreatment. The soluble sugars are there and they are not being used. The enzymatic hydrolysis can be made with the same liquid fraction of the acid pretreatment but is necessary detoxified it with the purpose of eliminate the inhibitors compounds and use the soluble sugars of the plantain peel.

3.2.2 Autohydrolysis and enzymatic hydrolysis

During this process about 90% of the xylan is hydrolyzed. However, the glucose content in the hydrolysate is very low. After the enzymatic hydrolysis glucose concentrations are reached at 100 g/L. The main advantage of these pretreatment is that the only reactive is water, which makes it a very attractive pre-treatment compared to diluted acid. Although not using any type of acid, during this pretreatment it can also be seen the formation of inhibitory compounds as reported by Garrote et al. [46]. In the literature there are some works where it is evaluated a similar process, for example Romaní et al. [47] studied the influence of the hydrothermally pretreatment (or autohydrolysis) before an enzymatic hydrolysis for the Eucalyptus globulus, a final concentration of 82 g/L of glucose was obtained. Nunes and Porquie [48] reports a final concentration of 43 g/L of glucose after a steam explosion follow by enzymatic hydrolysis for eucalyptus wood. With these results it can be shown that autohydrolysis is a very effective pretreatment prior to enzymatic hydrolysis since it allows the degradation of much of the xylan to then be converted to glucose by the enzymes.
3.3 Technical assessment

In the four cases, the yields were calculated to evaluate technically each process. Table 2 shows the results. For both raw materials the best yield is for the ethanol production. In the case of butanol, the formation of other components like acetone, ethanol and some acids reduces the yield, because the glucose consumed by the microorganism goes to the production of these components. In the case of the plantain peel all the yields are lower. This occurs because the low quantity of sugars after the enzymatic hydrolysis. Other factor that can be influence the yields is the scale. In the high scale there are more sugars than in the low scale. However, not all of these are consumed.

<table>
<thead>
<tr>
<th></th>
<th>g ethanol/ g biomass</th>
<th>g ethanol/ g glucose</th>
<th>g butanol/ g biomass</th>
<th>g butanol/ g glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eucalyptus globulus</td>
<td>0.133</td>
<td>0.501</td>
<td>0.027</td>
<td>0.311</td>
</tr>
<tr>
<td>Plantain peel</td>
<td>0.052</td>
<td>0.332</td>
<td>0.007</td>
<td>0.292</td>
</tr>
</tbody>
</table>

Other aspect to analyze in these processes is the energy requirements. Figure 3 shown the inputs and outputs requirements for the ethanol and butanol process from plantain peel (Figure 3a) and Eucalyptus globulus (Figure 3b). In all the processes, the main energy consumption occurs in the separation zone. Although the butanol production process has a more complex separation scheme, it consumes less energy, since after the first distillation tower and the decanter the flow decreases considerably, requiring less energy for its processing. On the other hand, the production of ethanol shows a greater energy consumption, this is because the two single towers processes a greater amount of flow, requiring more energy. This is why for the plantain peel a flow of 0.264 ton/h of butanol and 1.327 t/h of ethanol are obtained. Moreover, for Eucalyptus globulus, 7.034 ton / h of butanol and 51.944 ton / h of ethanol are obtained. In both cases, it can be seen that the amount of ethanol is considerably higher than that of butanol. It means that to get the same amount of both products would require much more energy to produce butanol.

In figure 3a, it can be seen that for both products the energy required is greater than the energy released. This means that in these small-scale processes it is not possible to carry out an energy integration to benefit economically the process, so it could be thought that in the case of ethanol, more utilities will be required, which will increase the cost of the process. Figure 4a shows the results for the process with Eucalyptus globulus, which corresponds to high scale, the energy generated is greater than the energy consumed, allowing to made a scheme of energy integration and thus take advantage of the energy in the process streams. This may represent an advantage over low-scale processes by allowing the reduction of utility costs with the use of the generated energy. However, the values for the energy in the Eucalyptus case are very higher than in the plantain peel case.
3.4 Economic analysis

As a result, the economic analysis shows that in all cases the highest cost is the corresponding to raw materials, representing about 90% of total costs. This is because being lignocellulosic agroindustrial waste is required large quantities to obtain a good yield of sugars and the value product, to make the process viable. The second factor that most affects the cost of production are the utilities, as already mentioned above these are required mainly in the separation zone. In the case of the high scale, it could be done an energy integration to reduce the requirements of utilities and thus the cost associated with them. The general and administrative costs also have a considerable influence. The other costs evaluated for each process are shown in figure 4. The ethanol production from Eucalyptus is the most expensive process. The operating labor cost, maintenance cost and plant overhead has a similar value for the processes. The operating charges are the least valuable for the process.

![Figure 4. Economic results for each process](image)

To know the viability of each process the profit margins were calculated. For this, the commercial cost of the butanol and the ethanol was taken from [49]. The commercial value of butanol was 0.8 USD/kg and the ethanol 0.706 USD/kg. The results are in table 3.

<table>
<thead>
<tr>
<th>Butanol PP</th>
<th>Ethanol PP</th>
<th>Butanol EG</th>
<th>Ethanol EG</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.52</td>
<td>0.44</td>
<td>-1.26</td>
<td>0.43</td>
</tr>
</tbody>
</table>

For both cases of ethanol production the profit margin is positive, this means that the sales of the product manage to cover the total costs of production, although the value is close to zero. This value can increase as the process has more time in execution and is stabilizing, additionally some changes in the process as could be the energy integration in the case of eucalyptus would allow the increase of this margin. Butanol production cases have a negative profit margin, although the commercial value of butanol is higher. This is because the flows obtained from this product are very low, possibly the use of the energy released in the process allows to increase this value to make the process economically viable.

4. Conclusion

The use of lignocellulosic feedstocks as raw material to obtain biofuels gives an advantage to the process and allows increasing it economic viability. The plantain peel has many sugars that are diluted in the acid pretreatment and are waste. For this reason it is suggested not to separate the solid and liquid fractions until the end of the stage of obtaining sugars. This work allows to demonstrate that the ethanol production is a more cost-effective process than the production of butanol because the difference in the obtained flows. However, butanol has greater advantages over ethanol as a fuel because of its energy content. In all processes, the representative costs are those corresponding to raw materials and utilities. However, in the high-scale
processes, the costs of using the utilities decrease because better energy integration can be made to take advantage of the process streams.

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6. References


