

## COMPARED EXERGY ANALYSIS OF CELLULOSE HYDROLYSIS ROUTES

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**Abstract.** *The comparison of hydrolysis routes (acid and enzymatic) has become an important issue nowadays, being a part of ethanol production routes by renewable sources. This paper uses exergy as a tool to compare five hydrolysis routes and define, from a thermodynamic point of view, the most efficient one. The reactor analyzed involves pure hydrolysis of cellulose: cellulose into glucose. Results show that enzymatic hydrolysis is equivalent to concentrated acid hydrolysis when both use equivalent saccharification efficiencies, with 60.1-61.6% exergy efficiency for enzymatic hydrolysis, 59.2-60.7% for concentrated acid hydrolysis, superior than diluted acid one, with 47.8% exergy efficiency, indicating that saccharification efficiency is a relevant parameter in hydrolysis processes efficiencies.*

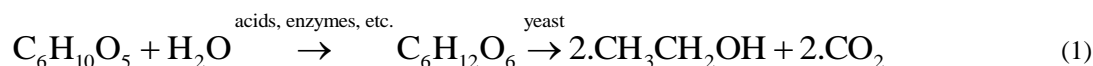
**Keywords:** *Exergy, biomass, concentrated acid hydrolysis, dilute acid hydrolysis, enzymatic hydrolysis.*

### 1. INTRODUCTION

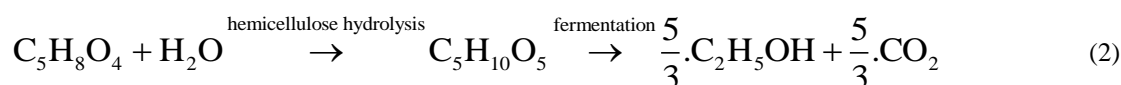
The exergy analysis is an assessment tool that provides alternative condition of analysis and comparison between processes in a rational form. Exergy can be seen as a measure of quantity and quality of the energy (Tan, Lee, Mohamed, 2010). Diminishing the exergy losses (potential of work), a process goes into the increment of the sustainable use of energy (Dincer, Rosen, 2007).

The burnt of fossil fuels is the major source of gases that causes the intensification of the greenhouse effect, resulting in changes of the world climate (IPCC, 2007). Meanwhile fossil fuels release carbon formed millennia ago, between other greenhouse effect gases, biomass absorbs carbon from atmosphere. In a pure economic basis, gasoline or diesel are far more competitive than biofuels, which need economic incentives or politic interventions. The technology involved in petroleum refining is mature and any drastic fluctuation is unlikely. Differently from fossil fuels, the price of bioenergy, especially from biofuels, has been diminishing with technological advancements and with a more robust demand in the market (Ghatak, 2011). Ethanol is the major product of biorefineries, used mainly as transport fuel.

Hydrolysis is a process in a biochemical route of ethanol production by biomass-sugar conversion. Lignocellulosic biomass is composed mainly of lignin, cellulose and hemicellulose, where cellulose and hemicellulose can be converted into sugars. There are two types of hydrolysis: hydrolysis of cellulose, to obtain glucose, which can be fermented into ethanol, or hydrolysis of hemicellulose, to acquire especially xylose, a C<sub>5</sub> sugar that cannot be fermented with high efficiency yet. Lignin is the outer part of biomass, hemicellulose is the middle part, and cellulose is the inner part: cellulose is the harder part to be processed for being the inner part of biomass. Meanwhile, hemicellulose is easier to be hydrolyzed (Ely, 2009). Therefore, to make hydrolysis of cellulose occur with a high efficiency, it is necessary to perform some pre-treatments on the biomass: mechanical, delignification (removal of lignin), and hydrolysis of hemicellulose. Nowadays there are several ways to accomplish pre-treatments, such as mechanical pre-treatment, physical, physical-chemical, chemical and biological, with variations, such as oxidizing agents, alkaline treatments, organic solvents, etc. (Kipper, 2009) that precede and influence hydrolysis of cellulose. The theoretical conversion for cellulose to glucose, and glucose to ethanol (along with carbon dioxide) is given by Eq. (1), constituting cellulose hydrolysis:



The theoretical conversion for hemicellulose to xylose and arabinose (monosaccharides containing five carbon atoms), and its conversion to ethanol is given by Eq. (2):



With respect of sugars and the respective number of carbons, sucrose is a C<sub>12</sub> sugar, found in the sugarcane broth; glucose, fructose and galactose are C<sub>6</sub> sugars (sucrose is a molecule of fructose united to a glucose one); xylose and arabinose are C<sub>5</sub> sugars. By hydrolyzing sugarcane bagasse, for instance, one acquires glucose from glucon (part of

cellulose), xylose from xylan, arabinose from arabinan and galactose from galactan, where xylan, arabinan and galactan are parts of bagasse hemicellulose (Cortez, 2010).

Figure 1, modified from Hamelinck and Faaij (2006), illustrates the complete route for ethanol production by fermentation and distillation of sugars obtained through biomass hydrolysis. The hydrated ethanol produced in the fermentation process is especially used to acquire anhydrous ethanol. Hydrolysis heightens the amount of ethanol produced: with the available technology, it can increase ethanol production of 12.3% in biorefineries (Palacios-Bereche et al., 2012).

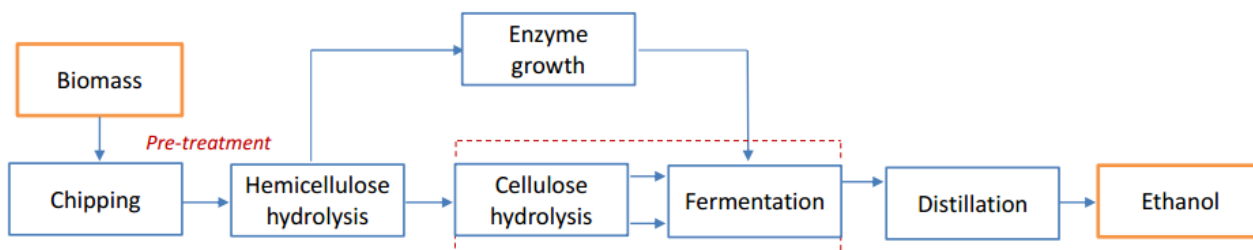


Figure 1. Ethanol production by hydrolysis fermentation schematically (Modified from Hamelinck and Faaij, 2006).

The focus of this article is the middle part of Fig. 1, cellulose hydrolysis. Pre-treatment is a very important part, and as hemicellulose hydrolysis, fermentation and distillation, it can change drastically the global efficiency of the processes. If it is desired the comparison between different cellulose hydrolysis processes, the focus must be in it when using exergy analysis, assuming the pre-treatment, preceding part, was successfully performed.

## 2. PROCESSES CHARACTERISTICS

The three different processes of hydrolysis studied, with their characteristics, are presented in Tab. 1.

Table 1. Studied hydrolysis routes: characteristics, advantages and disadvantages.

| <i>Hydrolysis route</i> | <i>Advantages</i>                                                                                                                                                      | <i>Disadvantages</i>                                                                                                     |
|-------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| Enzymatic               | Allows integration between hydrolysis of hemicellulose, cellulose and fermentation of C <sub>5</sub> and C <sub>6</sub> sugars, reducing costs and inputs <sup>1</sup> | High reaction period, implying high electricity consumption <sup>2</sup>                                                 |
|                         | Environmentally clean <sup>1</sup><br>Low maintenance costs <sup>1</sup>                                                                                               | Enzymes can be degraded in a high integrated process <sup>1</sup>                                                        |
| Concentrated Acid       | High saccharification is achievable <sup>2</sup><br>Small reaction time <sup>2</sup>                                                                                   |                                                                                                                          |
|                         | Accepts many acids, such as sulfuric acid, hydrochloric acid and nitric acid <sup>2</sup>                                                                              | Needs acid recuperation <sup>1</sup><br>High quantity of acids needed <sup>2</sup>                                       |
|                         | Low degradation level <sup>2</sup>                                                                                                                                     | Expensive anti-corrosive reactors <sup>3</sup>                                                                           |
| Dilute acid             | High saccharification is achievable <sup>2</sup><br>Small reaction time <sup>2</sup>                                                                                   |                                                                                                                          |
|                         | Accepts many acids, such as sulfuric acid, hydrochloric acid and nitric acid <sup>2</sup>                                                                              | Higher temperatures: higher demand of heat <sup>1</sup>                                                                  |
|                         | It is in a very advanced stage (since 1898), being a mature process <sup>4</sup>                                                                                       | Limiting saccharification efficiencies for cellulose hydrolysis (not low for mannose, xylose and galactose) <sup>1</sup> |
|                         | Uses a low quantity of sulfuric acid <sup>2</sup>                                                                                                                      |                                                                                                                          |

<sup>1</sup> Seabra (2008); <sup>2</sup> Hamelinck, Van Hooijdonk and Faaij (2005); <sup>3</sup> Ely (2009); <sup>4</sup> EERE (2007 apud Seabra, 2008).

The acid hydrolysis can hydrolyze both cellulose and hemicellulose, with a few differences in reaction time, quantity of acids and temperature in order to convert biomass into C<sub>6</sub> or C<sub>5</sub> sugars.

Regarding enzymatic hydrolysis, enzymes are denominated cellulases if they are produced by fungi, bacteria, etc. With enzymatic hydrolysis some process integration are possible: **SHF** (separate hydrolysis and fermentation), **SSF** (simultaneous saccharification and fermentation), **SSCF** (simultaneous saccharification and co-fermentation) and **CBP** (consolidated bioprocessing (Hamelinck, Van Hooijdonk and Faaij, 2005)).

Cellulose hydrolysis can be integrated with fermentation of C<sub>6</sub>, C<sub>5</sub> (co-fermentation), and with enzyme production. All these integrations are between hemicellulose hydrolysis and distillation (see Fig. 1).

### 3. MODELING DESCRIPTION

Five routes were chosen: one route with dilute acid hydrolysis, two with concentrated acid hydrolysis, and two with enzymatic hydrolysis. In this paper, it is assumed that 50 kg of water is in a reactor with 1 t of dry cellulose (concentration of cellulose of 2% (w/v) (Sun and Cheng, 2001)).

The chosen routes can hydrolyzate any kind of lignocellulosic biomass, such as sugarcane bagasse, banana fruit, wood residues, etc. (Velásquez, Ruiz and Oliveira Junior, 2009).

The saccharification efficiencies (mass conversion efficiency from cellulose to glucose) adopted are some of the best found nowadays (see Dedini Industries (2009) and Velásquez (2009)). To effectively compare concentrated acid and enzymatic hydrolysis, close efficiencies of saccharification were chosen for the routes (90 and 91.7%). An acid hydrolysis with a higher saccharification is better than an enzymatic hydrolysis with a small saccharification; the opposite is confirmed as well. The five routes in Tab. 2 present the operating temperature of the reactor, the reaction time, the quantity of sulfuric acid for acid hydrolysis and the expected saccharification. Data in Tab. 2 were compiled from Hamelinck, Van Hooijdonk and Faaij (2005); Rabelo et al. (2011); Inoue et al. (2005 apud Seabra, 2008)).

Table 2. Parameters of routes studied.

| <i>Parameters</i>                                               | <i>Route 1<sup>1</sup></i> | <i>Route 2<sup>1</sup></i> | <i>Route 3<sup>1</sup></i> | <i>Route 4<sup>2</sup></i> | <i>Route 5<sup>3</sup></i> |
|-----------------------------------------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Hydrolysis type                                                 | Dilute acid                | Concentrated acid          | Concentrated acid          | Enzymatic                  | Enzymatic                  |
| Saccharification efficiency                                     | 70%                        | 90%                        | 90%                        | 90%                        | 91.7%                      |
| Quantity of sulfuric acid relative to the mass of dry cellulose | 1%                         | 70%                        | 30%                        | -                          | -                          |
| Reaction time                                                   | 3 min                      | 6 h                        | 2 h                        | 90 h                       | 75 h                       |
| Reactor temperature                                             | 215°C                      | 40°C                       | 40°C                       | 90°C                       | 45°C                       |

<sup>1</sup> Hamelinck, Van Hooijdonk and Faaij (2005)

<sup>2</sup> Rabelo et al. (2011)

<sup>3</sup> Inoue et al. (2005 apud Seabra, 2008)

Figure 3 shows the scheme of the reactor where the process occurs. Heat is supplied to the reactor at an average temperature, T<sub>H</sub>, given by Eq. (3):

$$T_H = T_{\text{reaction}} + 10 \text{ K} \quad (3)$$

The reactor operates at 1 bar. Glucose is the product of the process. Residues, along with the non-converted cellulose are removed from the reactor. The average power required to agitate the solution is considered 2 kW. Heat losses to the environment are neglected.

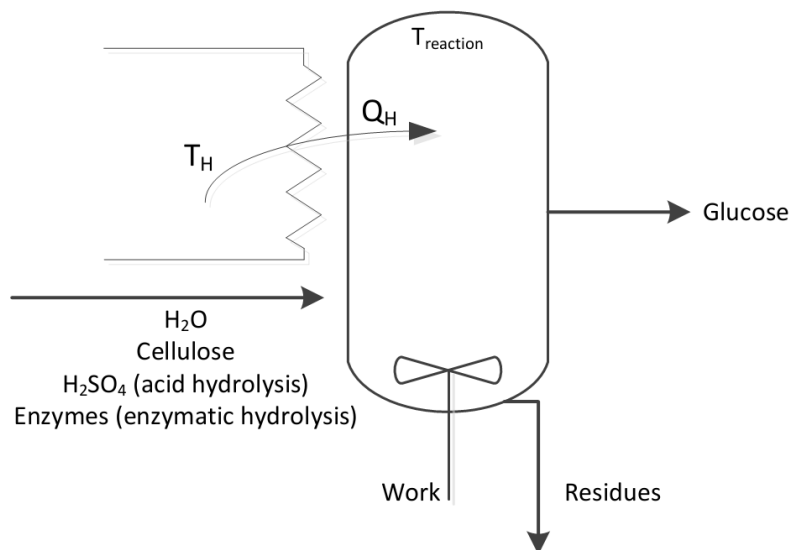


Figure 3. Diagram of cellulose hydrolysis reactor.

Glucose mass is calculated by Eq. (4), where  $\eta_{\text{saccharification}}$  is the saccharification reaction efficiency:

$$\eta_{\text{saccharification}} = \frac{m_{\text{glucose}}}{m_{\text{cellulose}}} \quad (4)$$

The mass balance of sulfuric acid, for acid hydrolysis, is achieved by Eq. (5):

$$m_{\text{H}_2\text{SO}_4} = m_{\text{cellulose}} x_{\text{H}_2\text{SO}_4} \quad (5)$$

The exergy balance of the reactor, for acid hydrolysis routes, is given by Eq. (6).

$$B_{\text{cellulose}} + B_{\text{H}_2\text{SO}_4(\text{Acid})} + B_{Q_H} + B_{\text{H}_2\text{O}} + B_{\text{electricity}} = B_{\text{ch,glucose}} + I \quad (6)$$

Where  $B_{\text{ch,glucose}}$ ,  $B_{\text{cellulose}}$ , and  $B_{\text{electricity}}$  are respectively the exergy of glucose syrup, cellulose, and electricity.  $B_{\text{H}_2\text{SO}_4}$ ,  $B_{Q_H}$ ,  $B_{\text{H}_2\text{O}}$  represents the exergy of sulfuric acid, heat supplied and water;  $I$  comprehends the irreversibilities.

The heat supplied exergy is calculated by Eq. (7),  $T_0$  is the temperature of the environment, adopted as 298.15 K.

$$B_{Q_H} = Q_H \left( 1 - \frac{T_0}{T_H} \right) \quad (7)$$

The exergy efficiencies were calculated, for acid hydrolysis, by Eq. (8), where the exergy of glucose is its chemical exergy.

$$\eta_b = \frac{B_{\text{ch,glucose}}}{B_{\text{cellulose}} + B_{\text{H}_2\text{SO}_4(\text{Acid})} + B_{Q_H} + B_{\text{H}_2\text{O}} + B_{\text{electricity}}} \quad (8)$$

The exergy analysis was performed using “Engineering Equation Solver” software (EES, 2011). Table 3 presents data required in the determination of the exergy balances and exergy efficiencies. In this table, LHV is the lower heating value,  $b_{\text{ch}}$  is the chemical exergy and MW is the molecular weight.

The exergy of cellulose ( $\text{C}_6\text{H}_{10}\text{O}_5$ ) was calculated based on its lower heating value (Eucalyptus Online Book and Newsletter, 2012), according to Eq. (9) from Kotas (1995), valid for dry solid fossil fuels with mass fraction ratio in the following range:  $2.67 > x_o/x_c > 0.667$ , including wood.

$$\frac{b_{ch}}{LHV} = \frac{1.0438 + 0.1882 \frac{x_H}{x_C} - 0.2509 \left( 1 + 0.7256 \frac{x_H}{x_C} \right) + 0.0383 \frac{x_N}{x_C}}{1 - 0.3035 \frac{x_O}{x_C}} \quad (9)$$

Table 3. Required data for exergy balances.

| <i>Substance</i>                                              | <i>LHV (kJ/kg)</i> | <i>b<sub>ch</sub> (kJ/kg)</i> | <i>MW (kJ/kmol)</i> |
|---------------------------------------------------------------|--------------------|-------------------------------|---------------------|
| Glucose<br>(C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> )   | -                  | 15504 <sup>2</sup>            | 180.16              |
| Cellulose<br>(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) | 18828 <sup>1</sup> | 22538.3                       | 162.14              |
| Enzymes                                                       | -                  | 3.47 <sup>2</sup>             | 42,000              |
| H <sub>2</sub> SO <sub>4</sub>                                | -                  | 1424.9 <sup>3</sup>           | 98.078              |
| H <sub>2</sub> O                                              | -                  | 42.74 <sup>3</sup>            | 18.015              |

<sup>1</sup> Eucalyptus Online Book and Newsletter (2012)

<sup>2</sup> Ojeda et al. (2011)

<sup>3</sup> Szargut (2012)

#### 4. RESULTS

Table 4 indicates the values of each term of Eq. (6), the required heat and electricity, the glucose mass and the destroyed exergy, for the production of 1 t of cellulose. Tab. 4 is based on values from Tab. 2.

Table 4. Mass and exergy balance of the analyzed routes.

| <i>Element</i>                                | <i>Route 1<br/>Dilute acid</i> | <i>Route 2<br/>Concentrated acid</i> | <i>Route 3<br/>Concentrated acid</i> | <i>Route 4<br/>Enzymatic</i> | <i>Route 5<br/>Enzymatic</i> |
|-----------------------------------------------|--------------------------------|--------------------------------------|--------------------------------------|------------------------------|------------------------------|
| m <sub>H<sub>2</sub>O</sub> (t)               | 0.05                           | 0.05                                 | 0.05                                 | 0.05                         | 0.05                         |
| B <sub>H<sub>2</sub>O</sub> (MJ)              | 2.14                           | 2.14                                 | 2.14                                 | 2.14                         | 2.14                         |
| m <sub>H<sub>2</sub>SO<sub>4</sub></sub> (t)  | 0.01                           | 0.7                                  | 0.3                                  | -                            | -                            |
| B <sub>H<sub>2</sub>SO<sub>4</sub></sub> (MJ) | 14.25                          | 997.5                                | 427.5                                | -                            | -                            |
| m <sub>cellulose</sub> (t)                    | 1                              | 1                                    | 1                                    | 1                            | 1                            |
| B <sub>cellulose</sub> (MJ)                   | 22538.3                        | 22538.3                              | 22538.3                              | 22538.3                      | 22538.3                      |
| m <sub>enzymes</sub> (t)                      | -                              | -                                    | -                                    | a                            | a                            |
| B <sub>enzymes</sub> (MJ)                     | -                              | -                                    | -                                    | b                            | b                            |
| Q <sub>heat supplied</sub> (MJ)               | 376.85                         | 44.66                                | 36.02                                | 127.98                       | 39.38                        |
| B <sub>heat supplied</sub> (MJ)               | 151.3                          | 3.46                                 | 2.78                                 | 25.72                        | 3.60                         |
| B <sub>electricity</sub> (MJ)                 | 0.36                           | 43.2                                 | 14.4                                 | 648                          | 540                          |
| m <sub>glucose</sub> (t)                      | 0.7                            | 0.9                                  | 0.9                                  | 0.9                          | 0.917                        |
| B <sub>glucose</sub> (MJ)                     | 11379.9                        | 14631.3                              | 14631.3                              | 14631.3                      | 14907.7                      |
| m <sub>residues</sub> (t)                     | 0.36                           | 0.85                                 | 0.45                                 | 0.15                         | 0.13                         |
| I (MJ)                                        | 11850                          | 9631                                 | 9031                                 | 9261                         | 8867                         |
| η <sub>b</sub> (%)                            | 47.8                           | 59.2                                 | 60.7                                 | 60.1                         | 61.6                         |

a 12.5 kg enzymes / t dry biomass (Velásquez, 2009);

b exergy of enzymes is 43.4 kJ.

Route 1, dilute acid hydrolysis, has the minor performance (a medium efficiency) due to the saccharification is lower than the respective value in other routes. Route 3, concentrated acid hydrolysis, has a higher performance than route 2 because it uses a lower quantity of sulfuric acid along with a smaller reaction time. Route 5, enzymatic hydrolysis, has a higher performance than route 4 for there is a higher saccharification, and smaller reaction time along with a lower reaction temperature, which gives smaller electricity. The electricity used in enzymatic hydrolysis is 12.5-45 times superior to concentrated acid hydrolysis because the reaction period is much longer, however the four last routes have high exergy efficiencies.

With the same inputs values for Routes 1 to 5, and using other saccharification efficiencies, it is possible to predict low hydrolysis exergy performances, and also theoretical future hydrolysis exergy performances (with 95-99.9% of saccharification efficiency). Joining all obtained results, Tab. 5 is formed:

Table 5. Exergy performances for current and future technology scenarios.

| <i>Saccharification efficiencies (%)</i> | <i>Exergy efficiencies (%)</i> |                                      |                                      |                              |                              |
|------------------------------------------|--------------------------------|--------------------------------------|--------------------------------------|------------------------------|------------------------------|
|                                          | <i>Route 1<br/>Dilute acid</i> | <i>Route 2<br/>Concentrated acid</i> | <i>Route 3<br/>Concentrated acid</i> | <i>Route 4<br/>Enzymatic</i> | <i>Route 5<br/>Enzymatic</i> |
| 50.0                                     | 34.1                           | -                                    | -                                    | -                            | -                            |
| 70.0                                     | 47.8                           | 46.0                                 | 47.2                                 | 46.8                         | 47.0                         |
| 90.0                                     | -                              | 59.2                                 | 60.7                                 | 60.1                         | -                            |
| 91.7                                     | -                              | -                                    | -                                    | -                            | 61.6                         |
| 95.0                                     | -                              | 62.5                                 | 64.1                                 | 63.4                         | 63.8                         |
| 99.9                                     | -                              | 65.7                                 | 67.4                                 | 66.7                         | 67.1                         |

Table 5 indicates that with 50% of saccharification the exergy efficiency is low, less than 35%. With 70%, the exergy efficiency is higher for dilute acid hydrolysis, 47.8%, because it uses a lower quantity of sulfuric acid and electricity relative to the other two hydrolysis processes. With 90-91.7%, exergy efficiencies arrive up to 62%, forming a high efficiency. And with 95-99.9% of saccharification efficiencies, it is noticeable that cellulose hydrolysis can have a medium-high exergy efficiency, not reaching 70%, destroying a considerable percentage of inputs exergies in the process (30%), also due to the chemical reactions involved.

Velásquez (2009) calculated the exergy efficiencies for banana hydrolysis, obtaining 51.3% and 57.4% for acid hydrolysis with 95.0% of saccharification efficiency; the author also used enzymatic hydrolysis, obtaining 20.3% of exergy efficiency with 55.0% of saccharification efficiency. Efficiencies reported are lower than those located in Tab. 5, because the author included the mechanical pre-treatment and delignification in hydrolysis control volume.

## 5. CONCLUSIONS

For the analyzed conditions it is possible to conclude that enzymatic hydrolysis possesses approximately the same quality of energy conversion process compared to concentrated acid hydrolysis with an equivalent saccharification value, both being superior to dilute acid hydrolysis of cellulose with the actual technology (because of the limiting saccharification efficiencies). Hydrolysis exergy efficiencies are function of saccharification mass efficiencies, and saccharification is a relevant indicator for hydrolysis processes efficiencies to choose between acid and enzymatic processes.

It must be taken into account that the implementation of acid hydrolysis reactors, even with a high saccharification, is depreciated by the high cost of equipment due to the necessary acid corrosion resistance, as Tab. 1 mentions; and that enzymatic hydrolysis, that is environmentally clean, allows the interaction between hydrolysis, fermentation of C<sub>5</sub> and C<sub>6</sub> sugars in schemes as simultaneous saccharification and co-fermentation, reducing the costs and some inputs values, seeming to be more attractive than concentrated acid hydrolysis, except for the fact of higher reaction time, having a superior demand of electricity compared to acid hydrolysis.

## 6. ACKNOWLEDGEMENTS

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