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Simulation of Dilute Acid Hydrolysis of Banana Waste for Ethanol Production: Comparison between the Use of Fruits, Peel and Pseudostem

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Banana waste has been used to produce bioethanol with the goal of developing a low-cost, sustainable production method. Brazil, which annually generates large amounts of agro industrial waste, has high technological potential in this area. The pseudostem, peel and the fruit can be used and studies are focused on the hydrolysis because it has been proven that this step involves the highest production cost. The goal of this study is to evaluate the acid hydrolysis of banana residues using simulation. It was used the Aspen HYSYS® software simulating the heating, hydrolysis, neutralization and cooling process, from experimental data previously evaluated. A conversion reactor was used and the reactions of cellulose to glucose and that to the hydroxymethylfurfural (HMF) were implemented. Calculation was made in order to obtain the conversion for the optimum conditions of previous work: 120°C, 2 % (weight) H_2SO_4 and residence time in reactor of 15 min. For these conditions a conversion of cellulose to glucose of 36 % can be obtained when pseudostem was used. Tests were performed with this value for three residues mentioned and then the conversion was increased gradually to the maximum value (100 %). Even known that the conversion of lignocellulosic residues is around 40-60 %, we aimed to corroborate the results previously obtained in the laboratory with data that have not been evaluated experimentally, as the energetic condition of the process and HMF production. The analysis of the energy consumption per sugar produced demonstrated that the hydrolysis of banana fruit residue (pulp) is unattractive as shown experimentally. This behaviour is independent of the increased conversion process. For hydrolysis of the pseudostem was observed that there is a decrease in the amount of energy required in respect of glucose produced to near 80 %, from which the gains with increasing conversion are few.

1. Introduction

The worldwide interest in obtaining sustainable energy for the future motivates the search for other means of energy production, as fossil fuels are becoming increasingly scarce. A number of nations are strategically organizing themselves to obtain new means of energy generation using various types of vegetal biomasses as sources of renewable energy, such as bioethanol. In Brazil, this fuel is produced through the fermentation of glucose and fructose obtained from the sucrose present in sugar cane. Although sugar cane has advantages as a raw material for ethanol production, and its use is well-established, the use of productive land for sugar cane instead of food crops has been questioned. For this reason, technological methods that enable the efficient production of bioethanol have been continuously sought for both economic and environmental reasons (Pereira, 2011).
Banana waste has been used to produce bioethanol with the goal of developing a low-cost, sustainable production method. The production of fuel alcohol from lignocellulosic biomass requires several distinct stages, including hydrolysis, which is highlighted because it is at this stage that the fermentable sugars become available for fermentation. There are various possible methods for this process, and the most commonly used methods can be classified into two groups: chemical hydrolysis and enzymatic hydrolysis (Taherzadeh and Karimi, 2007).

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The enzymatic route has been preferentially studied in recent years (Cannella et al., 2010), as it is performed under moderate conditions and does not produce undesirable byproducts. However, there is still a significant cost associated with the enzymes, and the enzymatic processes are complex. Thus, methodologies employing dilute acids have also gained prominence. In this process, the biomass is mixed with acid, generally sulphuric acid diluted in water (the catalyst), and heated for a specific time (Canilha et al., 2010). These dilute acid methodologies have important advantages, due to the low cost of the reagents and reduced restrictions in terms of intellectual property (Ribeiro, 2010). However, the disadvantage of these techniques is the formation of degradation compounds, such as furfural, hydroxymethylfurfural (HMF), and acetic acid, which are inhibitors of the organisms that produce ethanol from sugars (Drapcho et al., 2008).

The ethanol production process from banana cultivation waste is different from the production process from sugar cane and is still not well-known, making it necessary to evaluate the operational and energetic integration of the stages, such as hydrolysis. In this regard, a process simulation allows researchers to evaluate both variables that are difficult to obtain experimentally and the various stages of the process without the need to interfere with the process (Palacios-Bereche et al., 2011). Therefore, the objective of this study is to simulate the hydrolysis stage of bioethanol production from banana cultivation waste (pulp, peel and pseudostem) using the Aspen Hysys® simulator to investigate the energetic relationships among the sugar formed and the various conversions of cellulose to glucose.

2. Simulation

The process was simulated with the Hysys® software version 7.3, employing the following stages: mixture, heating, dilutes acid hydrolysis, cooling, neutralization and solid separation. This procedure was applied to the hydrolysis of the banana pulp, the peel wastes, and the pseudostem of the banana tree.

From simulations performed with sugar cane bagasse, Dias (2008) and Rodrigues (2007) suggested that the UNIQUAC model is the most appropriate. As banana cultivation wastes have many similarities to sugar cane, this model was considered to be appropriate and was employed in the subsequent simulations. Following the definition of the thermodynamic model, the necessary components were implemented for all of the reactions. It was necessary to create hypothetical components (those that are not present in the database of the simulator) according to the composition of the waste. The properties provided to the simulator for the hypothetical components (solid and liquid) are implemented according to Dias (2008).

Three inlet streams were inserted: the aqueous substrate (waste), sulphuric acid, and water for dilution. The mass fractions of the wastes were obtained from Gonçalves Filho (2011) for the pseudostem and Schulz (2010) for the pulp and peel. The non-quantified material was considered to be lignin in the simulations, as this material does not react in the process.

All of the equations used in this study were inserted as conversion reactions (based on stoichiometry). The conversions for the equations shown were utilized according to literature sources, which simulated the process with sugar cane bagasse. The conversion of cellulose hydrolysis to glucose started from 36%, which was the experimentally obtained value. For the reaction of hydroxymethylfurfural (HMF) it was used the conversion of 2 %, according to Dias (2008). An acid-base reaction was also considered for the neutralization stage, forming salt and water.

The inlet streams (aqueous waste stream, dilution water, and H_2SO_4) were mixed and heated to 120 °C using a heat exchanger and were later directed to a conversion reactor (Hydrolysis Reactor), where the hydrolysis reactions took place. The outlet streams of the reactor (gas and liquid) were mixed, cooled to 25 °C and subsequently sent to a neutralization reactor, where a base stream was added. The outlet streams of this reactor were directed to a solid separator to obtain a fermentation broth. It is worth mentioning.

The hydrolysis simulation was performed with three types of waste (pulp, peel, and pseudostem), considering the conversion reactions of cellulose (36 %) and the formation of HMF. The operational conditions were 120 °C after heating and 2 % sulphuric acid relative to the wet mass (WM) of the lignocellulosic substrate in the inlet. The stream inlet pressure of the hydrolysis reactor was set at 1.96 atm (198.6 kPa), as the stream is totally liquid at this value.

The experimental process was conducted in batches, but to implement the continuous simulation, the flow rates were calculated to obtain a residence time of 15 min, which was used experimentally. An inlet flow rate of 0.4 kg/h was determined, with 0.1 kg/h for the aqueous substrate (0.25 % solids in WM) as used experimentally, 0.002 kg/h for the sulphuric acid stream (2 % relative to the wet basis), and 0.298 kg/h for the dilution water (the amount required to complete the calculated flow rate). The mass fractions are shown in Table 1.

Table 1: The mass fractions used in the inlet stream for the simulation with the banana waste.

	Mass Fractions (Wet Basis)		
Components	Pseudostem	Peel	Pulp
Lignin	0.0187	0.0692	0.0972
Cellulose	0.0206	0.0218	0.0098
Hemicellulose	0.0077	0	0
Water	0.953	0.886	0.701
Sucrose	0	0.001	0.041
Glucose	0	0.011	0.078
Fructose	0	0.011	0.073

The inlet flow rate of the base in the neutralization phase was 1.599×10^{-3} kg/h. This value was obtained by varying the base in the simulator until all of the mass of acid was consumed, indicating complete neutralization. After performing the simulation with the 36 % conversion for cellulose, variations of this conversion were also evaluated at 50 %, 60 %, 70 %, 80 %, 90 %, and 100 %.

3. Results

Results of the quantities of energy necessary for heating and cooling in the simulations are shown in Table 2, and the mass flow rates of the products formed are shown in Table 3. In Table 4, it can be observed the amount of glucose in the input and output streams for each waste studied, and also the quantity that refers to the production of glucose in the simulation.

The data show that the energy consumed for heating and cooling the three wastes was similar. For the pseudostem, there was 0.00080753 kg/h (0.80753 g/h) of glucose in the outlet stream. This quantity, according to the yield calculations of 0.511 g of ethanol/g of glucose as obtained by Gonçalves Filho (2011), produces approximately 0.41 g of ethanol. The complete combustion of this quantity of ethanol can generate 11.152 kJ. Therefore, as expected, the energy balance for the production of ethanol from biomass is negative. It is important to note that in this case, only the hydrolysis stage was considered. Pimentel (2003) confirmed that the energy required for the production of a gallon of ethanol is approximately 29 % greater than the energy produced during combustion.

Table 2: The energy employed in the heating and cooling stages in the simulation of the pulp, peel, and pseudostem wastes with a 36% conversion in the reaction of cellulose to glucose and the reaction for the formation of HMF.

Energy (kJ/h)	Pulp	Peel	Pseudostem
Heating	154.4	158.8	159.5
Cooling	146.2	150.3	150.9

Table 3: The mass flow rates of the products formed in the simulation with a 36% conversion for the reaction of cellulose to glucose and the reaction for the formation of HMF.

Mass flow rate (kg/h)	Pulp	Peel	Pseudostem
Sucrose, Fructose and Glucose	0.0194282	0.0031326	0.00080753
Glucose	0.0080282	0.0019326	0.00080753
HMF	0.00011469	0.000027608	0.000011536
Cellulose	0.0006272	0.0013952	0.0013184
Hemicellulose	0	0	0.00077
Lignin	0.00972	0.00692	0.00187
Salt	0.0028377	0.0028377	0.0028377

Table 4: Amount of glucose in the input and output streams and the quantity produced in the simulation of the pulp, peel, and pseudostem wastes with a 36 % conversion in the reaction of cellulose to glucose and the reaction for the formation of HMF.

Glucose (g/h)	Pulp	Peel	Pseudostem
Input	7.80	1.10	0.000
Output	8.02	1.93	0.807
Produced (Output minus Input)	0.22	0.83	0.807

According to the findings of Rodrigues (2007), 769 kJ/kg were consumed to heat the sugar cane bagasse to 240°C. In the simulation, the heat required was 386 kJ/kg for the pulp, 397 kJ/kg for the peel, and 398.75 kJ/g for the pseudostem. The values from the simulation are on the same order of magnitude as those presented by the cited author, considering that the biomass in this study was heated to 120°C.

Based on Table 4, it was observed that the quantity of glucose in the outlet stream is greatest for the pulp; however, in terms of glucose production, the pseudostem produced the most. This result is due to the quantity of this sugar that is already present in the inlet stream for the hydrolysis of the pulp and peel. There is initially 0.0011 kg/h of glucose in the peel substrate stream, and there is 0.00193 kg/h in the outlet, which corresponds to an increase of approximately 75.6 %. For the pulp, there is 0.0078 kg/h of glucose in the inlet and approximately 0.00802 kg/h in the outlet, corresponding to an increase of only 2.925 %. For the pseudostem, there is no glucose in the inlet stream and a total of 0.00087 kg/h in the outlet; therefore, this type of waste produced the most glucose.

Regarding the HMF production (Table 2), it was observed that approximately 0.000115 kg/h (mass fraction of 2.86×10^{-4}) was formed from the pulp, and this value was the largest one obtained for the three wastes. This behavior was expected, as HMF formation is related to the quantity of glucose present in the media because HMF is a byproduct formed from the decomposition of glucose due to the high temperatures of the hydrolysis process (Dias, 2008). It is known that the inhibitory effect of HMF occurs at concentrations greater than 0.25 g/L (Harmsen et al., 2010), that is, at a mass fraction of approximately 0.00025. In the simulations, the HMF mass fractions were lower than the inhibitory concentration, approximately 0.00003 for the pseudostem and 0.000069 for the peel. Thus, under the conditions employed in the process, the production of HMF is not sufficient to promote inhibition during the later fermentation of the wastes. In the case of the pulp, the HMF mass fraction was 0.000286; therefore, inhibition occurs. However, as this value is highly similar to the inhibitory concentration, a more critical evaluation would be necessary to confirm that inhibition occurs. It is important to emphasize that HMF forms during long hydrolysis times. Therefore, shorter times are preferred for this process to avoid the formation of this inhibitor. Besides, it is important to mention that in the sequence of unit operation of bioethanol process, the fermentation section is placed after cellulose hydrolysis to glucose section. Inhibitors crucially condition the fermentation process, so it is necessary to consider the advantages and disadvantages of enzymatic hydrolysis or the dilute acid process. For enzymatic, it is necessary to perform a cost analysis of enzymatic hydrolysis, because in this case the presence of inhibitors is lower and the overall process is definitely improved. Also, the acid hydrolysis even used in pseudostem, could have the disadvantages of a neutralization step.

The energy consumption was also evaluated for this stage when the reaction conversion was varied for the formation of glucose. Different conversions were utilized to evaluate various cases that could not be studied experimentally. Figures 1 and 2 show the results for the energy consumption as a function of the quantity of sugar formed and the quantity of glucose for each waste (pulp, peel, and pseudostem), as the reaction conversion is varied from 36 % to 100 %. There are various studies related to the achievement of higher conversions; for example, Taherzadeh and Karimi (2007) evaluated the conversions of cellulose for different types of reactors and demonstrated that, depending on the reactor, larger or smaller conversions can be obtained.

As shown in Figures 1 and 2, as the reaction conversion increased for the pseudostem, the quantity of sugars that were formed decreased relative to the consumption of energy. This behavior was expected, as the consumption of energy changes little in relation to the conversion; that is, the quantity of sugars formed increases, whereas the energy consumption is not altered as significantly. It demonstrated that this material would be the best waste to be hydrolyzed, as there is a lower ratio between the consumption of energy and the sugar and glucose formed in addition to not having sugars available in natura.

The best results are for 100% conversion, which has a lower ratio for the energy consumption per quantity of sugars formed. However, 100 % conversion is not feasible. Nogueira (2008) has reported that the hydrolysis with dilute acid has yield limits between 50 % and 70 %. Furthermore, according to Schulz

(2010), the limiting factor in the hydrolysis process is the access of the catalyst molecules to the cellulose molecules. One of the main controlling factors of this access is the association of cellulose with hemicellulose and lignin. Santos et al. (2012) state that the difficulty of converting lignocellulosic biomass to chemical precursors is attributed to the chemical characteristics and morphology of the biomass. For example, cellulose has a structure that is highly resistant to destructuring, and for this reason, increasing the yield of the conversion of cellulose to glucose is not so simple.

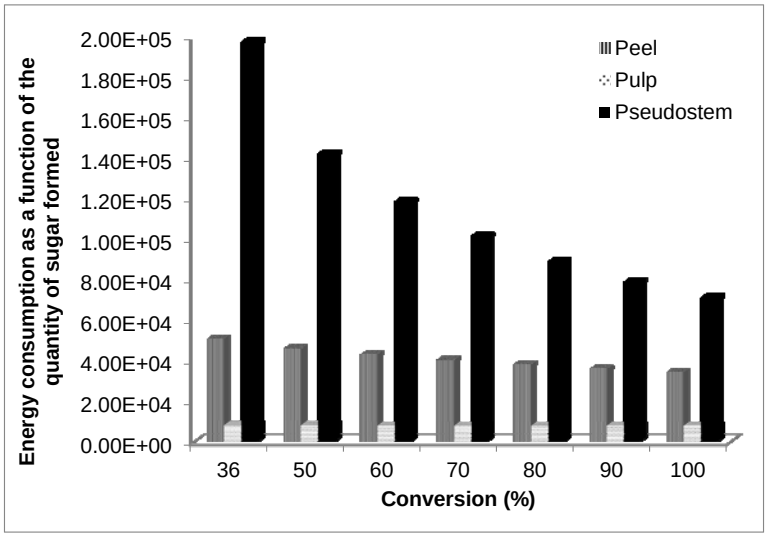

Figure 1: The energy consumption per quantity of sugar formed with conversions from 36 to 100 % for the hydrolysis of pulp, peel, and pseudostem wastes.

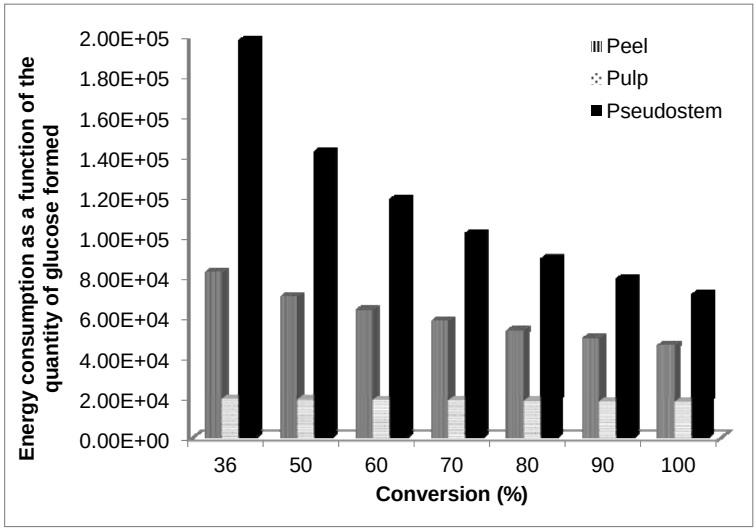

Figure 2: The energy consumption per quantity of glucose formed with conversions from 36 to 100 % for the hydrolysis of pulp, peel, and pseudostem wastes.

It was determined that the analysis performed for the pseudostem does not apply to the pulp and peel, as the ratio of energy consumption to the quantity of sugar or glucose is almost unaltered by an increase in conversion. This phenomenon occurs because the pulp already has a large quantity of free sugars prior to hydrolysis. According to Schulz (2010), the use of heating to 120°C for 15 minutes without the addition of acid increased the total sugar yield by 21 % to 26 %, and after the addition of acid, the concentration of sugars increased by only a few percentage points; therefore, the use of this type of treatment is not justified. That is, the quantity of glucose formed by the hydrolysis of the cellulose is low in relation to the quantity of sugars that are already available in the pulp prior to hydrolysis. The energetic analysis confirms

the experimental conclusion that the hydrolysis of the pulp is not viable, as the process consumes large quantities of energy for little sugar formed.

When only the energy consumption is analyzed in the hydrolysis of the peel for the quantity of glucose, this process is promising, but when all of the available sugars are evaluated, it is not favorable. This finding indicates that little sugar is formed in relation to the initial in natura quantity; thus, the hydrolysis is not promising because the energy consumption is large in relation to the quantity of sugars produced. For the pseudostem, the values do not change depending on the analysis performed because all of the sugar formed from this waste is accounted for as glucose; this finding is different from what occurs with the pulp and the peel, which also have sucrose and fructose.

4. Conclusions

In the simulation of the hydrolysis of the pulp, peel, and pseudostem wastes, the energy consumed was approximately 300.6 kJ/h for the pulp, 309.1 kJ/h for the peel, and 310.4 kJ/h for the pseudostem. The pseudostem was the most efficient glucose producer, producing approximately 0.87 g/h. For the analysis of the HMF formed, it was found that the greatest production was for the pulp (mass fraction of 2.86×10^{-4}), indicating that there is inhibition by this compound for the process with this waste. The ratio of energy consumption to quantity of sugars and glucose formed showed better results for the pseudostem, and this material is the best waste product for hydrolysis because the greatest quantity of sugar is formed in relation to the energy consumed.

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