

Evaluation of mass loss of pineapple bagasse pretreated with alkaline hydrogen peroxide**Avaliação da perda de massa de bagaço de abacaxi pré-tratado com peróxido de hidrogênio alcalino**

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ABSTRACT

In this work, the mass loss caused by the pre-treatment, with alkaline hydrogen peroxide, of the dried and ground pineapple bagasse was studied. The bagasse was separated granulometrically. The fractions with an average diameter of 1.242 mm (20 mesh) and 0.564 mm (48 mesh) showed the highest volumes among the sieves used. For this reason, these two fractions were chosen to evaluate the influence of particle size on the mass loss during the pre-treatment. The dry pineapple bagasse was characterized for the contents of moisture, ash, soluble and insoluble lignin, cellulose and hemicellulose, and carbohydrates. Central composite rotatable designs were carried out for each particle size in order to assess the influence of pre-treatment time (h), temperature (°C) and concentration of alkaline hydrogen peroxide (%) on the mass losses caused in the samples. The mass losses observed in the pineapple bagasse fractions, after pretreatment, varied between $80.467 \pm 0.722\%$ and $89.495 \pm 0.985\%$ for the 20 mesh bagasse and $79.641 \pm 0.856\%$ and $88.576 \pm 0.170\%$ for the 48 mesh bagasse. Mass losses were very high, which may indicate that pretreatment with alkaline sodium hydroxide is too aggressive for pineapple bagasse.

Keywords: Ethanol 2G, Biofuel, Biomass.

RESUMO

Neste trabalho foi estudada a perda de massa ocasionada pelo pré-tratamento, com peróxido de hidrogênio alcalino, do bagaço de abacaxi seco e moído. O bagaço foi separado granulometricamente, e as frações de diâmetro médio de 1,242 mm e 0,564 mm apresentaram os maiores volumes dentre as peneiras utilizadas. Por esta razão estas duas frações foram escolhidas e denominadas de 20 e 48 mesh respectivamente, com o objetivo de avaliar a influência do tamanho da partícula na perda de massa durante o pré-tratamento. Foi realizada a caracterização do bagaço de abacaxi seco moído quanto a umidade, cinzas, lignina solúvel e insolúvel, quantidade de celulose e hemicelulose, e carboidratos. Foram realizados planejamentos do tipo delineamento composto central rotacional para cada granulometria a fim de avaliar a influência do tempo de pré-tratamento (h), temperatura (°C) e concentração de peróxido de hidrogênio alcalino (%) nas perdas mássicas ocasionadas nas amostras. As perdas mássicas observadas nas frações do bagaço de abacaxi, após o pré-tratamento, variaram entre $80,467 \pm 0,722\%$ e $89,495 \pm 0,985\%$ para o bagaço de 20 mesh e $79,641 \pm 0,856\%$ e $88,576 \pm 0,170\%$ para o bagaço de 48 mesh. As perdas de massa foram muito altas, podendo indicar que o pre-tratamento com hidróxido de sódio alcalino é muito agressivo para o bagaço de abacaxi.

Palavras-chave: Etanol 2G, Biocombustível, Biomassa.

1 INTRODUCTION

Brazil is a prominent producer of biofuels from lignocellulosic biomasses. One of the most studied biomasses is sugarcane bagasse. However, a bagasse from any vegetable source have the potential to be the new raw material for ethanol 2G. There are advantages in using bagasse to produce biofuels. The material is already processed, reducing de costs with

transport. They are available in large quantities and are considered waste. They are usually applied as animal feed or soil enrichers. Although, they can have a much more value worth application as biofuel raw material (OLIVÈRIO & HILST, 2005; SCHIEBER et al., 2001; REZZADORI et al., 2012).

Brazil is one of the world leaders in fructiculture and was the 3^o in the world in pineapple production in 2018 (SHAHBANDEH, 2020). The majority of production is directed to *in natura* consumption (97%). About 40% of the processed fruit is considered bagasse, consisting of peel and some pulp. This waste is high in simple sugars but also in lignocellulosic material. As much as 40% is hemicellulose and 30% cellulose (GIL & MAUPOEY, 2018; ARUNA, 2019). Still, as a lignocellulosic material it is necessary to pretreat the material to make the cellulose available for hydrolysis.

The pretreatment is the first step in producing biofuels, especially for enzymatic hydrolyses. It removes the lignin and reduces the recalcitrance, exposing the cellulose for saccharification. However, the pretreatment can reduce de sugars output if it is inadequate. If it is too severe, it can remove part of the cellulosic material. Nevertheless, if it is too mild, it will not appropriately expose the cellulose for hydrolyses (CANDIDO et al., 2019; CAO et al., 2016). For these purpose the aim of the present work was to evaluate de carbohydrate composition of the pineapple bagasse and the mass loss caused by the alkaline hydrogen peroxide pretreatment.

2 MATERIALS AND METHODS

2.1 BIOMASS

The raw material was pineapple bagasse (pulp and peel) of white pearl variety, provided by Doce Vida fruit pulp industry, located in Anápolis-GO, Brazil. The bagasse was dried in an oven for three days at 60°C. Afterwards it was milled and sieved. The largest amounts were in the fractions of average diameter 1.242 mm (20 mesh) and 0.564 mm (48 mesh). Thus, these fractions were chosen to be studied. The bagasse was stored in the freezer for the duration of the study.

2.2 BIOMASS CHARACTERIZATION

The characterization of both bagasse granulometries was done applying the following methodologies: ash and moisture contents by Instituto Adolfo Lutz's (Adolfo Lutz Institute) (1976) methodology; soluble and insoluble lignin contents using the preconized by IUPAC as

described by Oliveira (2012); cellulose and hemicellulose contents by Browning (1967); carbohydrate content by High Performance Liquid Chromatography (HPLC). For the HPLC the bagasse underwent an acid hydrolyses. The hydrolyzed portion was tested in a LC-20A Prominence Shimadzu chromatographer, with a SUPERCOGEL Ca column, coupled to a refraction detector. Deionized water was the carrier solvent with a pump flow of 0.5 mL/min. The injection volume was 20 μ L and the oven temperature 80°C (OLIVEIRA, 2012). Analysis were done in triplicates.

2.3 PRETREATMENT WITH ALKALINE HIDROGEN PEROXIDE

The pretreatment followed an experimental design. The mass loss was evaluated by means of central composite rotatable design in three levels. The experiments consisted of 2³ assays of investigation with 3 replicas in the central point, and 6 experiments in the axial points (α) resulting a total of 17 experiments done in triplicates. The factors studied were reaction time (h), temperature (°C), and concentration of alkaline hydrogen peroxide (% v/v), the response being the mass loss. Bagasse samples of 4.0 g in dry basis for the 20 and 48 mesh fractions were put in Erlenmyer flasks and 100 mL of H₂O₂ solution was added. The pH was then adjusted to 11,5 with sodium hydroxide solution (20 mol/L) (KRISHNA, 2000). The concentrations of H₂O₂, time and temperature, according to the experimental design, are presented in Table 1. The tests were run in a shaker under orbital agitation of 150 rpm. After the appropriate times the residue was filtered and washed with deionized water until the filtered solution presented a 7.0 pH.

Table 1 – Coded and uncoded values for the pretreatment variables.

Variable	Values				
	- α	-1	0	+1	+ α
Time (h)	2.55	8	16	24	29.45
Temperature (°C)	9.77	20	35	50	60.23
[H ₂ O ₂] alkaline	0.64	2	4	6	7.36

Source: The authors

2.4 DETERMINATION OF MASS LOSS

The pineapple bagasse mass loss caused by the pretreatment was determined using Equation 1, where m_i is the inicial bagasse mass and m_a is the mass after pretreatment.

Equation 1

$$\text{Mass loss (\%)} = \frac{m_i - m_a}{m_i} \times 100$$

3 RESULTS AND DISCUSSION

3.1 BIOMASS CHARACTERIZATION

The results from both granulometries were statistically compared using Student's t-test at 90% confidence level. The comparison between the results of both granulometries show the concentrations of glucose, xylose, arabinose, cellulose and hemicellulose were equal with 10% significance. This shows the milling does not affect the global composition of the raw material. For that matter, the moisture and ash contents were done of the whole bagasse resulting in 12.82±0.04% moisture and 2.37±0.47% ash.

The pineapple bagasse's carbohydrate profile presented reducing and non-reducing sugars (Table 2). Both fractions had sucrose (non-reducing sugar) as the most abundant monomer. Previous studies show sucrose glucose and fructose can reach up to 80% of the carbohydrate levels in pineapple (GUTIERREZ et al., 1976). Aziz et al. (2011), found, in pineapple juice, sucrose levels close to this work (42.2 g/L).

Table 2: Characterization of both granulometries of pineapple bagasse

Components	20 mesh	48 mesh
Sucrose (%)	40.75 ± 0.69	44.75 ± 0.61
Glucose (%)	34.57 ± 1.60	29.28 ± 2.06
Xylose (%)	20.67 ± 0.62	20.67 ± 0.62
Cellobiose (%)	Non detectable	0.01 ± 0.00
Arabinose (%)	4.01 ± 0.22	4.18 ± 0.90
Total lignin (%)	23.03 ± 0.43	22.57 ± 0.86
Cellulose (%)	38.5 ± 0.82	36.7 ± 0.95
Hemicellulose (%)	35.9±0.39	33.4±0.44

Source: The authors

When it comes to total lignin content, sugarcane has around 23.0% (GOMES et al., 2015). Pineapple bagasse, in the present work, had similar values, which are considered low (BELKACEMI et al., 1998). The 20 and 48 mesh biomasses had, respectively, 22.03% and 22.57% of total of lignin. Since sugarcane is an interesting raw material to produce 2G ethanol, these results may indicate pineapple bagasse as a prominent biomass in this area.

The cellulose and hemicellulose fractions we found in this work were higher than the ones in other works with pineapple bagasse. Silva (2011) quantified 31.69% cellulose and 38.18% hemicellulose using the same methodology. Another work found cellulose levels ranging from 25.23% to 27.58% (MANEINTR et al., 2018). These differences in results could be explained by the fact that the vegetable cells' composition vary depending on the weather and location of crops (BANERJEE et al., 2018; DETROY & JULIAN, 1983).

3.2 DETERMINATION OF MASS LOSS AFTER THE PRETREATMENT

The mass loss results were statistically analyzed using the software STATISTICA 7.0 considering a 90% level of significance. The results (Table 4) show that the lowest levels presented the lowest mass losses. Accordingly, the highest mass losses occurred in the higher levels. Alkaline pretreatments are commonly applied in paper production. It is known to cause high cellulose losses, but it leaves straighter fibers, which is good for paper production (WOICIECHOWSKI et al., 2020). However, it may represent a low output is sugars, but also save resources. Since it requires low concentrations, time and temperatures to remove the lignin effectively.

Table 4: Matrix of the factorial experimental design 2^3 with coded and actual values and mass loss for 20 and 48 mesh pineapple bagasse.

Assay	Time (h)	Temperature (°C)	[H ₂ O ₂] (%)	Mass loss (%) 20 mesh	Mass loss (%) 48 mesh
1	8 (-1)	20 (-1)	2 (-1)	83.182±0.567	83.493±0.227
2	8 (-1)	20 (-1)	6 (1)	87.085±0.394	87.754±0.045
3	8 (-1)	50 (1)	2 (-1)	84.815±0.153	83.909±0.344
4	8 (-1)	50 (1)	6 (1)	89.495±0.985	87.351±2.081
5	24 (1)	20 (-1)	2 (-1)	85.034±1.561	84.376±0.041
6	24 (1)	20 (-1)	6 (1)	86.466±2.332	88.576±0.170
7	24 (1)	50 (1)	2 (-1)	84.593±1.395	84.339±0.368
8	24 (1)	50 (1)	6 (1)	88.464±1.392	88.456±0.393
9	2.55 (-1.68)	35 (0)	4 (0)	84.243±1.133	87.816±0.177
10	29.45 (1.68)	35 (0)	4 (0)	85.674±0.909	87.028±0.583
11	16 (0)	9.77 (-1.68)	4 (0)	85.133±0.597	87.354±0.125
12	16 (0)	60.23 (1.68)	4 (0)	87.078±1.495	88.176±0.007
13	16 (0)	35 (0)	0.64 (-1.68)	80.467±0.722	79.641±0.856
14	16 (0)	35 (0)	7.36 (1.68)	89.153±1.672	86.510±0.707
15	16 (0)	35 (0)	4 (0)	86.763±1.736	85.055±1.598
16	16 (0)	35 (0)	4 (0)	87.426±0.614	87.545±0.032
17	16 (0)	35 (0)	4 (0)	87.265±0.497	86.300±0.953

Source: The Authors.

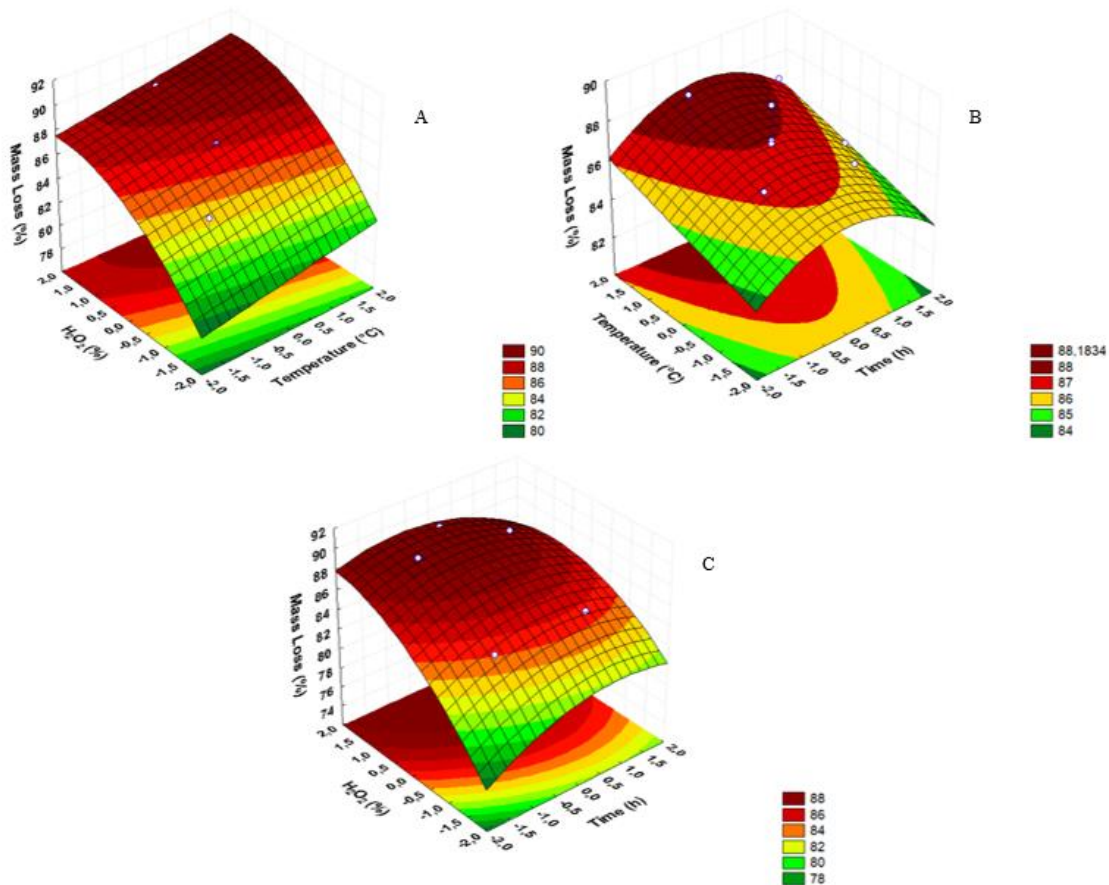
The statistical analysis of the 20 mesh mass loss returned a reduced model with the significant variables (Equation 2, where t is time, T is temperature and C is concentration of

hydrogen peroxide). Said model had a correlation coefficient (R^2) of 0.87, indicating a low replicability by the model. Figure 1 displays the response surfaces for the adjusted model. The surfaces reinforce the tendencies in table 1. The lowest conditions caused the lowest mass losses. It is also perceivable that time had little to no effect in the overall results. Time and concentration in the studied conditions were much more significant.

Equation 2

$$Y = 86,89 - 0,5153t^2 + 0,64T + 2,08C - 0,56C^2$$

Figure 1: Mass loss percentage response surface as a function of concentration and temperature (A); temperature and time (B); and concentration and time (C) of the acid saccharification of 20 mesh pineapple bagasse.



Source: The authors

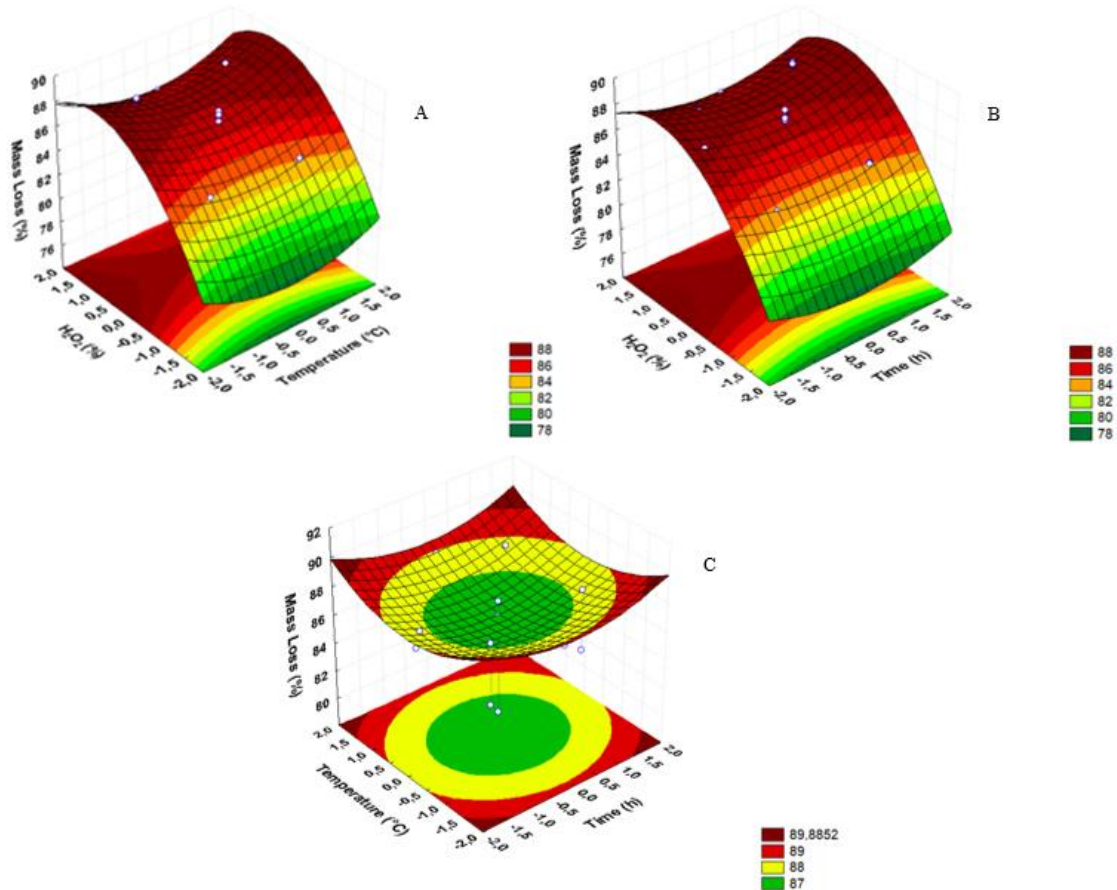
The same statistical analysis was done for the 48 mesh data. After the adjustments and selection of the significant factors, the reduced model's (Equation 3) R^2 was 0.94. This set of data results resulted a better model adjustment. Figure 2 presents the response surfaces for the interactions among the studied factors. The findings are similar to the ones for 20 mesh results.

The lowest levels of concentration and temperature yielded the best results. Time was not a significant factor as well.

Equation 3

$$Y = 86,3 + 0,38t^2 + 0,50T^2 + 2C - 1,14C^2$$

Figure 2: Mass loss percentage response surface as a function of concentration and temperature (A); concentration and time (B); and temperature and time (C) of the acid saccharification of 48 mesh pineapple bagasse.



Source: The authors

Odisi (2013) observed the mass loss of sugarcane bagasse pretreated with alkaline hydrogen peroxide and hydrogen peroxide supplemented with bagasse ash. The alkaline hydrogen peroxide pretreatment had losses around 35% of the hemicellulosic fraction. The losses for the ash supplemented one were around 10%. The author inferred that the alkaline pretreatment is too aggressive, degrading the hemicellulose and cellulose polymers as well as the lignin. We had mass losses over 70% for both fractions for the pineapple bagasse. It may be the pineapple bagasse is vulnerable to the severity of the alkaline hydrogen peroxide

pretreatment. It is also possible that hemicellulose and cellulose fractions were lost in the process.

4 CONCLUSION

The pineapple bagasse had a total lignina content close to what is found in sugarcane bagasse. Its cellulose and hemicellulose contents were higher than what is usually found for sugarcane bagasse. The carbohydrates found were sucrose, glucose, xylose, cellobiose, and arabinose. There was not a significant difference between the results for 20 and 48 mesh bagasse.

The mass loss for all the studied conditions was higher than 70%, indicating the alkaline hydrogen peroxide was too severe for the pineapple bagasse. Time was not a significant factor for the experimental design results. The results indicate further studies as necessary to find the optimal pretreatment for pineapple bagasse.

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