Study of Orange Bagasse Digestibility by Chemical Pretreatments

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The search for sustainable energy resources has to pass by the waste. Thereby it will be possible to solve two great problems: the increasing necessity for energy and the waste discard. Inside this reality, the lignocellulosic materials seem to be a good option to produce liquid biofuels. Specifically to Brazil, one of the biggest orange juice producers, the orange bagasse might be a candidate. The first step to study the potential of a new material to produce bioethanol is analysed its performance in the pretreatment. Hence this is the objective of this work. It was studied, based on a 2^3 factorial design, the mass loss of the orange bagasse submitted to lime and alkaline hydrogen peroxide pretreatments. The two higher mass loss for the calcium hydroxide were 72.03 % and 71.30 % achieved with 80 °C and 40 h, and for the alkaline hydrogen peroxide the better results were 61.12 % and 60.00 % in 24 h and with 0.6 mm particle size.

1. Introduction

One of the major issues the society deals is the question concerned energy. Nowadays, this problem seems to be more and more bigger due to the fact that not only is it necessary to supply the increasingly amount of energy the modern life needs, but also to develop environmentally friendly energy sources. In an attempt to solve this matter, investments have been made in the bioethanol production especially from sugarcane and corn. After some years of the usage of these raw materials, problems with it were raised. Among all, the necessity to enlarge the sugarcane and corn fields appears constantly associated with the cause of both increasing the spoil natural environment and reducing area of food cultivation. Furthermore the discussions become worst since some of the resources employed in the production is part of the human feed. As an answer of these new questions, efforts have been directed to evolve the second generation of bioethanol. On the contrary of the raw materials of the first generation, lignocelluloses are considered agricultural and industrial waste. Thus their usage is an utterly good proposal of a sustainable production which valorise materials that only have been faced as a problem to dump. In addition the lignocelluloses are by far the most abundant, renewable materials on the biosphere (Kuhad et al., 2011) and they are not concentrated in just few regions of the Earth as fossil fuels are (Hahn-Hagerdal et al., 2006).

Basically, the technique to product bioethanol of second generation consists of four paths: pretreatment, hydrolyse, fermentation and distillation. Since the lignocellulosic materials are recalcitrant, the first step is extremely important to enhance the cellulose digestibility and consequently increasing the efficiency of the process and diminishing the costs (Rabelo et al., 2011). Among pretreatments, the alkaline ones have considerable advantages. They present effectiveness to delignification and depolymerise the cellulose as well as they have less costs and energy need (Ghosh et al., 2012). Moreover the calcium hydroxide is cheaper than others alkalis and the alkaline hydrogen peroxide does not leave residuals in the biomass (Rabelo et al., 2011).

According to the ideas presented, this study has the target of investigating the potential of orange bagasse to produce bioethanol. The orange bagasse is the main waste produced by the orange juice industry. It is about 40 % of the fruit mass (Santos et al., 2000). Thereby the research was carried out based on a 2^3

factorial design (Rabelo et al., 2011) for both alkaline hydrogen peroxide and calcium hydroxide pretreatments. Varying the temperature, the time and the particle size, the efficiency of the pretreatments was analysed by the loss mass.

2. Materials and Methods

2.1 Preparation of bagasse
The orange bagasse was provided by juice industry Gyn Fruit, located in Goiânia-Brazil. Before store the biomass, it was dried in an oven at 60 °C for 72 h and cooled until the environment temperature. Then it was crushed, sifted and kept in containers.

2.2 Pretreatment

2.2.1 Calcium hydroxide
Samples of 2 g of biomass were treated with 0.5 g of $Ca(OH)_2$ in 50 ml of distillated water. Then they were put in a shaker configure with 150 rpm. The temperature and time of the reaction were established by the factorial design.

2.2.2 Alkaline hydrogen peroxide
Samples of 2 g of biomass were treated with 50 ml of H_2O_2 3 % (v/v), adjusting the pH to 11.5 by adding NaOH. Then they were put in a shaker configure with 150 rpm. The temperature and time of the reaction were established by the factorial design.

2.3 Factorial design
A factorial design 2^3 with two central points and two replicate for each experiment (Seolatto et al., 2012) was employed. The value of the levels was established based on the literature for two pretreatments (Rabelo et al., 2011).

2.3.1 Calcium hydroxide design
The table 1 shows the factors and levels chosen.

Table 1: Factors and levels for the calcium hydroxide

Factors	Level value /Central point value	Representation
Particle size (mm)	0.6	-1
	2.0	1
	1.3	0
Time (h)	20	-1
	40	1
	30	0
Temperature (°C)	60	-1
	80	1
	70	0

2.3.2 Alkaline hydrogen peroxide design
The Table 2 displays the factors and levels chosen.

Table 2: Factors and levels for the alkaline hydrogen peroxide

Factors	Level value /Central point value	Representation
Particle size (mm)	0.6	-1
	2.0	1
	1.3	0
Time (h)	6	-1
	24	1
	15	0
Temperature (°C)	20	-1
	60	1
	40	0

2.4Efficiency of pretreatment

The mass loss occurred during the pretreatment was used as a response and calculated conform Eq(1).

$$mass\ loss = \frac{raw\ bagasse - pretreated\ bagasse}{raw\ bagasse} \times 100\ \%$$ (1)

3. Results and discussion

The experiments were realized as stated by the factorial design and the planning matrix with the results is showed in the Table 3 and Table 4.

Table 3: Experimental loss mass to calcium hydroxide pretreatment where PS is particle size, t is time, T is temperature and ML is mass loss.

Exp.	PS	t	T	ML (%)
1	1	-1	-1	58.94
2	1	1	-1	62.14
3	-1	-1	-1	57.91
4	-1	1	-1	63.55
5	1	-1	1	67.67
6	1	1	1	71.30
7	-1	-1	1	67.40
8	-1	1	1	72.03
9	0	0	0	67.80
10	0	0	0	67.63

Table 4: Experimental loss mass to alkaline hydrogen peroxide pretreatment where PS is particle size, t is time, T is temperature and ML is mass loss.

Exp.	PS	t	T	ML (%)
11	1	-1	-1	44.50
12	1	1	-1	51.37
13	-1	-1	-1	38.08
14	-1	1	-1	60.00
15	1	-1	1	56.40
16	1	1	1	54.42
17	-1	-1	1	53.56
18	-1	1	1	61.12
19	0	0	0	50.92
20	0	0	0	51.80

A multiple regression analysis was conducted for both pretreatments on the software Statistica 7.0. As shown by analysis of variance (ANOVA) (Table 5), the time and temperature are the only effects not neglected for calcium hydroxide pretreatment with a significance level greater than 95 % (p<5 %).
Thereby the equation that represents the linear model was determined Eq(2) with a coefficient of determination R^2 = 97.3 %.

$$ML = 27.62 + 0.213t + 0.4478T$$ (2)

The independency from particle size is a desirable characteristic (Gómez et al., 2010) as the method does not demand energy to mechanical operation.
Since regression coefficients are positive for both time and temperature, it is properly to expect that bigger amount of loss mass will occur with the highest temperature and time of reaction. Analysing the Table 3, it can be seen that maximum loss mass truly happen in experiments with superior levels (6 and 8 which were submitted at 80 °C and 40 h of reaction). The Figure 1 illustrates this relation.

Table 5: Analysis of variance (ANOVA) for the calcium hydroxide

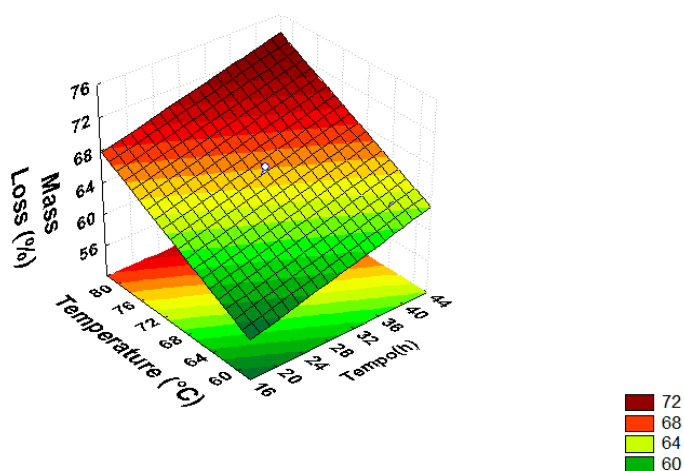| Sources of variation	Degrees of Freedom	Sum of Squares	Mean Square	F value	p
PS	1	0.18	0.18	0.08	0.78
t	1	73.06	73.06	31.81	0.00
T	1	321.22	321.22	139.84	0.00
PS*t	1	2.95	2.95	1.28	0.27
PS*T	1	0.00	0.00	0.00	1.00
t*T	1	0.09	0.09	0.04	0.84
G*t*T	1	0.52	0.52	0.23	0.67
Error	12	27.56	2.30		
Total	19				

Figure 1: Response surface diagram of the mass loss as function of time and temperature for calcium hydroxide.

Studying Figure 1, it is possible to conclude that the bigger efficiency (darkest area) is achieved in high temperature and time. Rabelo et al. (2011) found the same result in sugar cane bagasse research. According to the analysis of variance (ANOVA) (Table 6) for the alkaline hydrogen peroxide, the relevant parameters were the particle size, the time, the temperature, the interactions between time and temperature and time and particle size with a significance level greater than 95 %.

Table 6: Analysis of variance (ANOVA) for the calcium hydroxide

Sources of variation	Degrees of Freedom	Sum of Squares	Mean Square	F value	p
PS	1	2.67	2.67	0.42	0.52
T	1	249.48	249.48	39.06	0.00
T	1	294.81	294.81	46.16	0.00
PS*t	1	118.70	118.70	18.58	0.00
PS*T	1	4.97	4.97	0.78	0.38
t*T	1	104.04	104.04	16.29	0.00
G*t*T	1	1.85	1.85	0.29	0.59
Error	12	76.65	6.39		
Total	19				

In that way the equation that represents the linear model was determined (Eq(3) with a coefficient of determination R^2=98.5 %.

$$ML = 19.40 + 1.57t + 0.438T + 6.23PS − 0.016tT − 0.4877tPS \qquad (3)$$

To clarify the effects of the variables in the efficiency of the pretreatment, the response surfaces relating the particle size and time are showed below Figure 2.
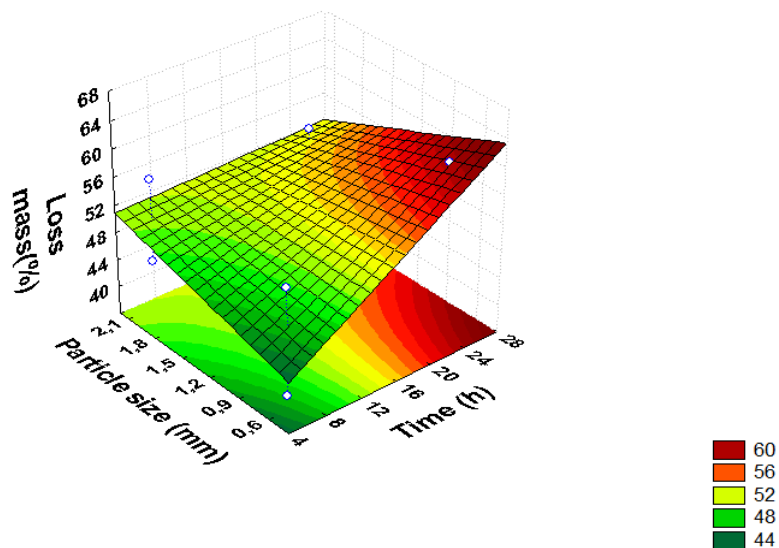

Figure 2: Response surface diagram of the mass loss as function of time and particle size for alkaline hydrogen peroxide.

From this figure it is possible to see that the alkaline hydrogen peroxide presented better performance at high time and small particle size.

Comparing the experiments 14 and 18 which differed just in the level of temperature and had the biggest mass loss it can be realized that the temperature had a smaller effect in the response than the other factors. As a result the alkaline hydrogen pretreatment can be performed at ambient temperature. This observation has a relevant importance for the viability of the process since it means lower cost with energy.

Comparing the results achieved in this work with those Rabelo et al. (2011) reached for the sugarcane: the maximum mass loss was 48.7 % in the alkaline hydrogen peroxide at 6 h, 60 °C and 5 % (v/v) of H_2O_2; for the calcium hydroxide the higher mass loss was 45.1 % at 54 h, 80 °C and 0.25 g(lime)/g(dry biomass), it is possible to infer that these pretreatment may have better performance with the orange bagasse rather than the sugarcane one.

4. Conclusions

The performance of the two pretreatments in the delignification was efficient: the mass loss was majority above 50 %. Other aspect that make these process viable for orange bagasse is the fact that their energetic demand is diminished by the no-dependency from particle size in the case of calcium hydroxide and the possibility to carry out the alkaline hydrogen peroxide in environmental temperature with effectiveness.

Despite that the bagasse pretreated with calcium hydroxide presented slightly more mass loss than the one submitted to the alkaline hydrogen peroxide pretreatment, it is not properly to state that the second is less indicated to treat the orange bagasse. Before conclude something like that, it is essential to do the hydrolysis of the cellulose in order to quantify the glucose (fermentable sugar). Regardless of this fact the study indicated that the orange bagasse may be a promising raw material for bioethanol production.

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