# Two Steps Chemimechanical Pulping Of Sugar Cane Bagasse Employing Acetic Acid

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*ABSTRACT*

*Acetic acid was used as pre- treatment chemical agent for the production of chemimechanical pulp from sugar cane bagasse. The process variables were, the acetic acid quantity from 20 to 60 % over the dry weight bagasse in each one of the two steps, temperature of 80 and 90$^0$ C and treatment time from 30 to 180 minutes. The depithed bagasse was cooked with acetic acid and 0.05 % hydrochloric acid as catalytic agent in polyethylene bags, heated by means of a temperature controlled water bath and using a 3,5:1 liquid-to-bagasse ratio. After the first step the cooked bagasse was defibrated in a Sprout-waldron disk refiner till 25-30$^0$ SR were reached, and after the second cooking step, 60$^0$ SR were obtained. With 30 % acetic acid in the first step, 50 % in the second one, at 90$^0$ C and 120 minutes for both steps, pulp characteristics were: breaking length 2.36 Km, tear 2.79 mNm$^2$ /g, brightness 36.5 % Elrepho and light scattering coefficient 32.3 m$^2$ /Kg. Some bleaching were made using hydrogen peroxide in one and two steps, with and without acetic and formic acid treatments between bleaching steps; the final brightness after 3 % hydrogen peroxide in two bleaching steps was 50.6 %, 53.3 % with acetic acid treatment, and 53.8 % Elrepho with formic acid treatment between steps.*

## INTRODUCTION

Studies on pulping processes with organic solvents have been made, according to Aziz (1), from more than 70 years ago, some of them, employed to produce chemical and semichemical pulps, whether using only organic solvents or mixed with another chemical agents (2-5). In the case of processes for high yield pulps, some studies have been made on chemimechanical pulps from sugar cane bagasse using methanol (6-8), but none about the use of acetic acid. That is why, the objective in this work, is to make a study on the process variables to produce chemimechanical pulps from sugar cane bagasse using acetic acid as a pre-treatment.

## EXPERIMENTAL

### Depithing

Whole bagasse with a pith content of 30%, was screened in an 8 thread/in. Wire mesh, then was steeped for 24 hours and treated in a Sprout-Waldron disk refiner with a 0.08 in. gap with tap water flow. The defibrated bagasse was screened again in the same mentioned mesh, obtaining a residual pith content of 17 % approximately.

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### Cooking

37 experiments with two cooking steps were made in polyethylene bags, heated by means of a temperature controlled water bath, with acetic acid variable quantities from 20 to 60 % over the sugar cane bagasse dry weight in each step, an 0.05 % hydrochloric acid was added as reaction catalyst, a temperature rate of 80 and 90° C was used and the treatment time was from 30 to 180 minutes. The second cooking step was made after the defibration of the bagasse in the disk refiner. During the two cooking steps a 3.5 to 1 liquid-to-bagasse ratio was used.

### Defibration and refining

After the first cooking step, bagasse was thoroughly washed with hot water (50° C), and then defibrated in a 12 in. diameter disk refiner with a pulp consistency of 5 % with an initial gap of 0.04 in. until 25-30° SR were reached, after this, the second cooking step was made. The refining was made in the same disk refiner until 60° SR were reached.

### Sheets making

Refined pulp was screened in a diaphragm equipment, with a 0.15 mm slot plate, paper sheets for strength and optical tests were made in a semiautomatic sheet former machine, 255/SA model from Testing Machines Inc. using the T-205 TAPPI test method.

### Pulp bleaching

The bleaching of pulps was made in different steps, using 0.4 % DTPA in the pretreatment, with pulp consistency of 5 % at room temperature for 30 minutes, then pulp was washed and squeezed. Each bleaching was made in polyethylene bags with 30 gr. of pulp, adding 0.2 % magnesium sulphate, 5 % sodium silicate 40° Be, 1 % sodium hydroxide and varying the peroxide quantity from 2 % to 3 %, in one or two steps, at 10 % pulp consistency, a temperature of 70° C, and the treatment time of 120 minutes. Some pulps were treated before or after peroxide bleaching, or between both steps, with 50 % acetic or formic acids at the same bleaching conditions.

## RESULTS AND DISCUSSION

### Pulp yield

The pulp yield obtained in this process is inversely proportional to the acetic acid quantity used in both steps, as the quantity of acetic acid is increased from 30 to 120 %, distributed in two steps, pulps yield reduces from 94 to 83 % respectively for the acid quantity limits **(fig.1).** Two reaction mechanisms for the acetic acid pulping have been proposed, the first one is an acid hydrolysis for the lignin and carbohydrates; and the second, is a solution of lignin fragments in the cooking liquor (9), supported in the fact that acetic acid is a source of hydronium ions which accelerate hydrolysis, and is a solvent for the lignin fragments (10).

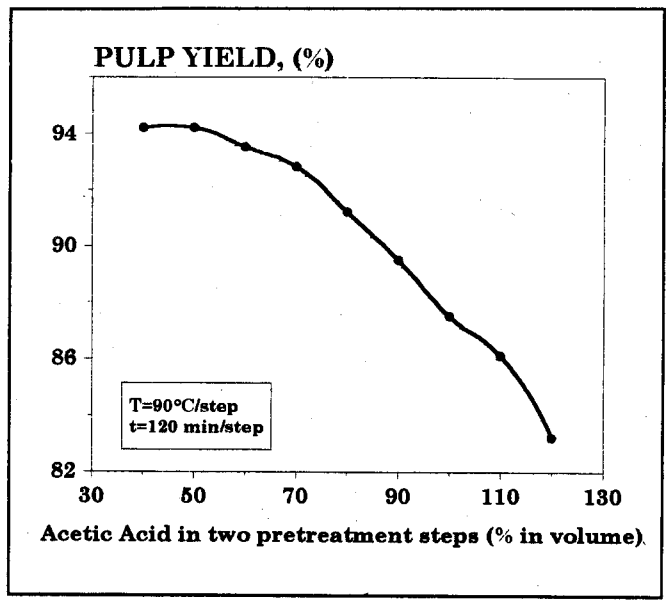


**Fig. 1 Effect of Acetic acid quantity in two pre-treatment steps on the pulp yield**

Although, solubility of lignin and carbohydrates were not analysed, it is believed that certain selectivity for the first one exists, due to the fact that acetic acid hydrolyses hemicelluloses slowly, obtaining a high content of them in the pulps (11). Also, it is indicated that organic acids, in this case, acetic acid, improve hemicellulose retention during the pulping process, because organic acids slow down fibre swelling, where carbohydrates predominate (4), so accessibility of chemical reagents in reduced inside them (12). Apostol and Koslov (13), have shown that the swelling degree observed

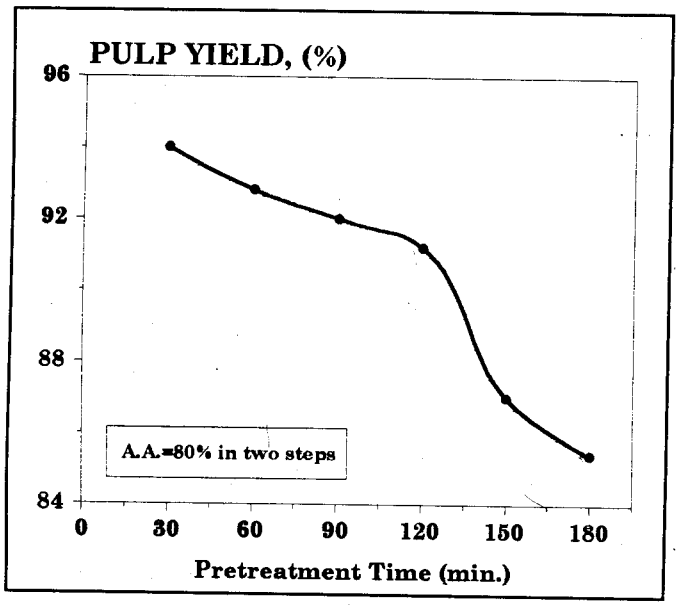


**Fig. 2 Effect of pre-treatment time variation in two steps on the pulp yield.**

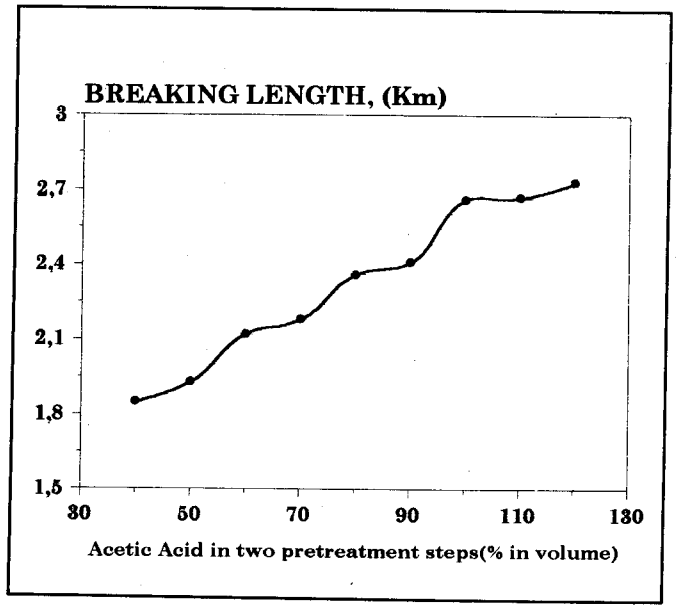


**Fig. 3 Effect of the Acetic Acid quantity in two pre-treatment steps on the pulp breaking length.**

in wood chips which had been impregnated with acetic acid is reduced as acid concentration is increased, however, in the other side, it is indicated that acetic acid is an excellent solvent, so, it is a good swelling agent for the solutions of lignin; for this reason, reduction in swelling belongs only to carbohydrates. making them less accessible to hydrolysis and solution (14).

Acetic acid is an extremely weak nucleophilic, for this reason, it is assured that acetylation of lignin is improbable, but it facilitates hydrolysis, so the key to eliminate lignin with acetic acid is the solution of its fragments, though is also indicated that there is a remote possibility of lignin acetylation (14), which has been verified by De Groote et al. (15), who say that during acetic acid-water pulping of sugar cane bagasse they obtained partially acetyled lignin with low molecular weight, and with 3 phenylpropane units approximately, associated with covalent bonds and with an acetyl group by monomer.

In the other side, when treatment time is increased from 30 to 180 minutes, a yield reduction is obtained, from 94 to 85.4 %, **(Fig.2)**. Young et al. (14). found that increasing treatment time from 1 to 4 hours, kappa number decreased and pulp yield showed the same tendency, but they also found, that at time over 4 hours, both increased, probably due to the lignin precipitation in pulp, at long treatment time.

## Breaking Length

The pulp tensile strength, represented by breaking length in **figure.3**, continuously increases as acetic acid quantity is increased from 30 to 120 % in volume distributed in the two steps, a maximal strength of 2.73 Km is obtained. The results seem to be in contradiction with the pointed out that blockading hydroxyl groups in fibres by means of sterification, it is shown in a strength reduction in pulps, due to the direct capacity reduction of hydrogen bonding between fibres and a fibre swelling reduction (16), Davis et al. (10), point out that their pulping results suggest that acetic acid pulps are more rigid, breakable and easier to be cut or broken during the defibration process. In other side, Herdle and Griggs (17), say that acetylation process facilitates disintegration more than fibrillation during refining process, because it makes fibres to be hydrophobic. However, Higgins et al. (16), found that paper strength from beaten and acetyled pulps is increased only in a low substitution degree, and over this point, it decreases, the reason is that only a few acetyl groups open

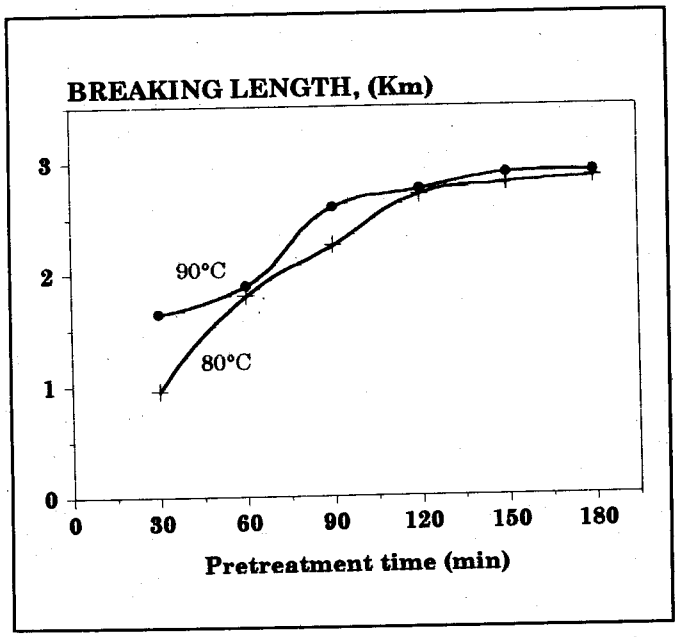


**Fig. 4 Effect of pre-treatment time variation in two steps on the pulp breaking length.**

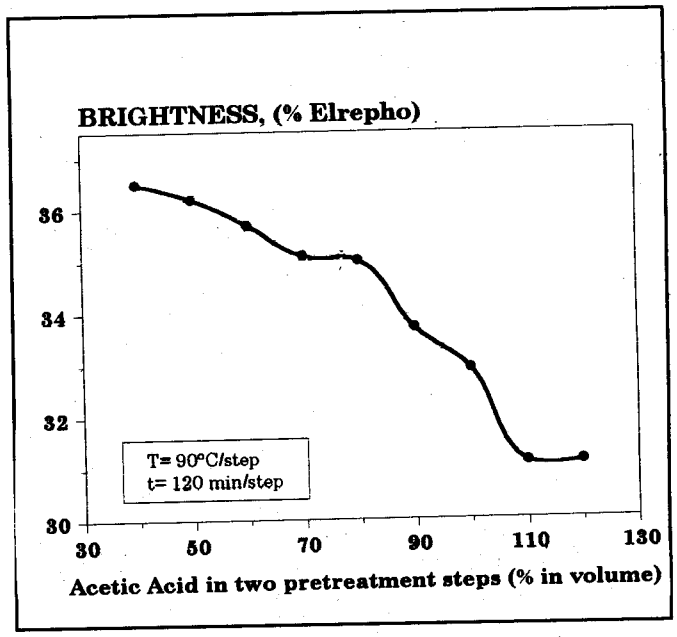


**Fig. 6 Effect of Acetic acid quantity in two pre-treatment steps on the pulp brightness.**

the fibre structure and provoke hydrogen bonds between hydroxyl groups near acetyl groups, facilitating moisture absorption, the last affirmation is based on the fact that the swelling rate passes from a maximum to a low degree during substitution. Herdle and Griggs (17), affirm that when just a few of acetyl goups are introduced into cellulose, water absorption is increased. Klinga et al. (18). Explain

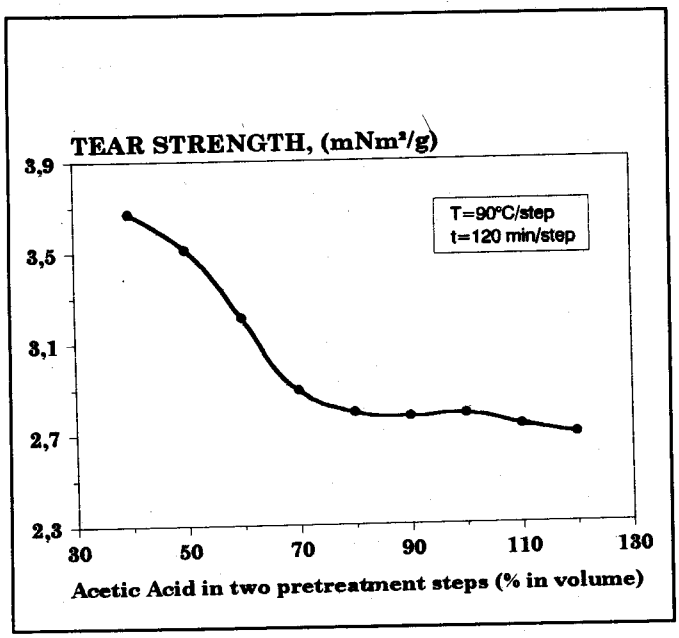


**Fig. 5 Effect of Acetic acid quantity in two pre-treatment steps on the pulp tear strength.**

the strength increase, in this case, because of the crossed unions formation, due to the formation of hemiacetal, between hydroxyl and carbonyl groups.

The continuous increment in tensile strength is based on the fact that as acetic acid quantity is increased during pulp treatment, specific volume is continuously decreased. Also increments in treatment time increase the related characteristic and in a lower proportion, temperature increments show the same effect **(fig.4)**, where values obtained at 90° C are lightly higher than the ones obtained at 80° C. Davis et al. (10), affirm that higher reaction temperatures seem not to affect pulp strength, except, because of the indirect effect of a lower kappa number obtained.

## Tear strength

Tear strength depends more on treatment time than on reagents quantity, increasing in the first case and reducing in the second. With an increment in the acetic acid quantity from 30 to 120 % distributed in the two cooking steps, tear strength is reduced 26%, from 3.67 to 2.69 $mNm^2/g$, **(fig.5).** The rigidity of the acetic acid pulp, makes fibres being easy to be cut or broken, reducing fibre length and tear strength. In other side, if treatment time is increased from 30 to 180 minutes, tear strength is

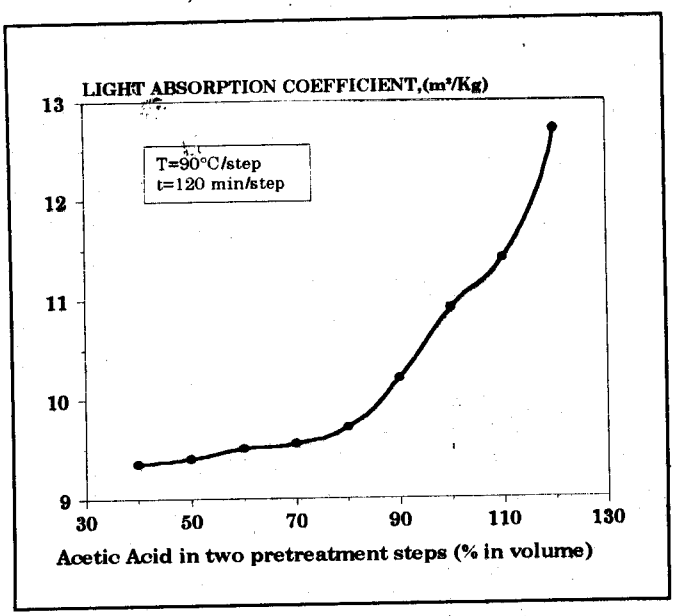


**Fig. 7 Effect of Acetic acid quantity in two pre-treatment steps on the pulp light absorption coefficient.**

increased almost 57 %, from 2.39 to 3.75 $mNm^2/g$ at 90° C, and over 184 % at 80° C, from 1.28 to 3.64 $mNm^2/g$, in relation to this, Herdle and Griggs (17), indicate that tear strength of partially acetyled pulps is significantly better.

### Brightness of unbleached pulps

Pulp brightness is reduced when acetic acid quantity is increased during treatment in both steps,

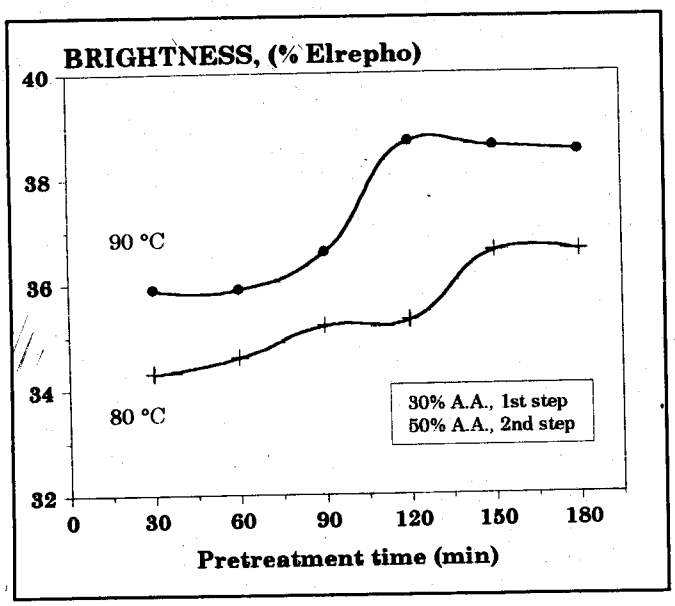


**Fig. 8 Effect of pre-treatment time variation in two steps on unbleached pulp brightness.**

increasing acetic acid quantity from 30 to 120 %, brightness is reduced about 15 %. from 36.5 to 31.1% Elrepho. **(fig.6)**, this behaviour is strengthened by a continuous light absorption coefficient increment, as acetic acid quantity is increased **(fig.7)**, probably, lignin precipitation is favoured, or some chromophoric groups are formed under the employed conditions.

By the other side, an increment in treatment time, with 30 % acetic acid during the first step and 50 % during the second one, increases brightness about 7 % at 90° C and a little over 7 % at 80° C, increasing from 34.3% to 36.6 % in the first case and from 35.9 % to 38.5 % Elrepho in the second case, as can be observed in **fig.8,** Young et al. (17) also found that increments in treatment

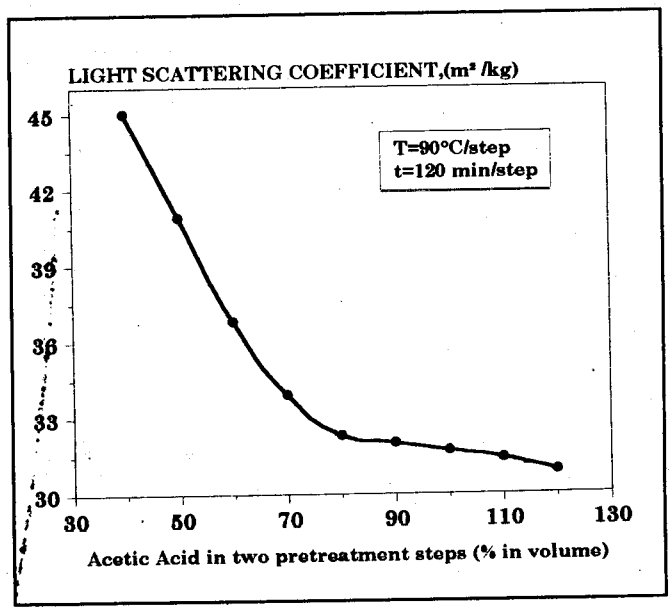


**Fig. 9 Effect of acetic acid quantity in two pre-treatment steps in the pulp light scattering coefficient.**

time produce light decrements in kappa number.

### Light scattering coefficient

The light scattering coefficient of the pulps obtained with acetic acid in two steps is continuously reduced when the acid quantity is increased, **(fig.9).** Likewise, increments in treatment time reduce such characteristic as much at 80° C as at 90° C, reducing over 24 and 25 % respectively. Values in both temperatures are very close during time increments,

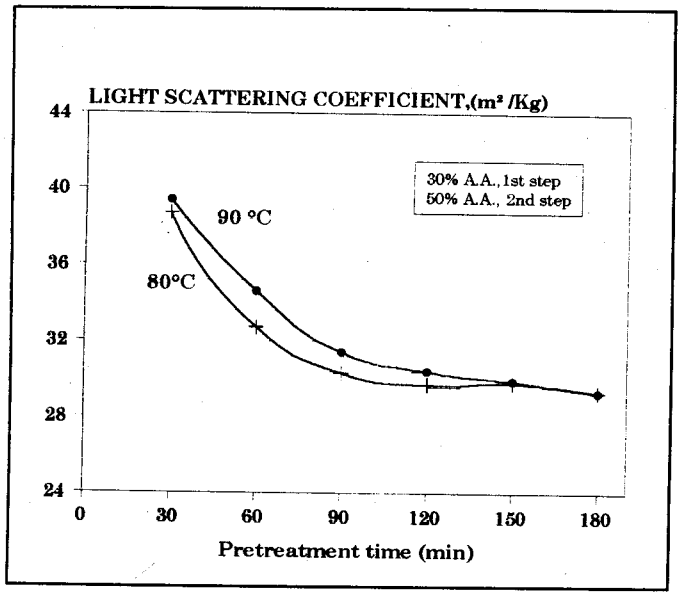


**Fig. 10 Effect of pre-treatment time variation in two steps on the pulp light scattering coefficient.**

they are practically the same at time over 120 minutes **(fig.10).**

**Peroxide bleaching and acetic and formic acid treatments.**

The bleaching conditions and the obtained results appear in table I, in which we can observe that using 3 % peroxide, the obtained brightness is only 47.7 % Elrepho, but distributing peroxide in two

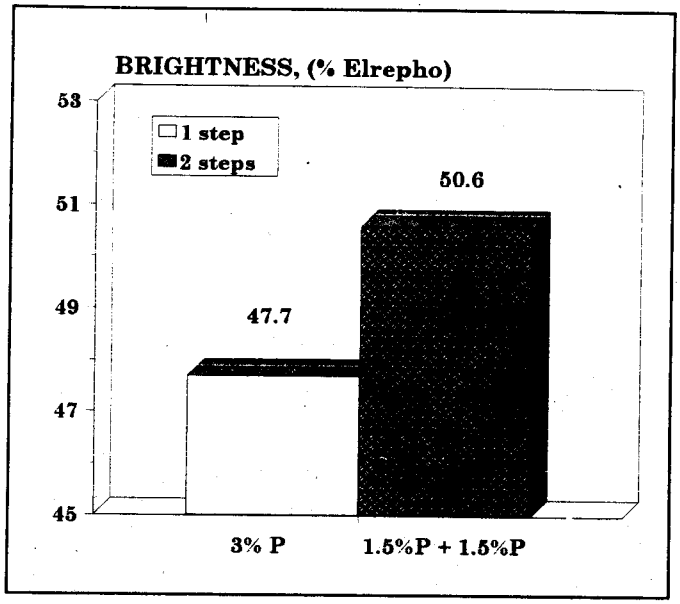


**Fig. 11 One and two steps bleaching influence on the acetic acid bagasse pulp brightness.**

bleaching steps, the brightness is increased 2.9 percent, obtaining a final brightness of 50.6 % Elrepho **(fig.11).**

Using 3 % peroxide in one step and giving a posterior pulp treatment with 50 % acetic acid at the same bleaching conditions, the brightness increases from 47.7 % to 50.5 % Elrepho, and 51.3 % Elrepho if formic acid instead of acetic acid is used. By other side, using 3 % peroxide distributed in 2 % and 1 % steps, and also, with an intermediate

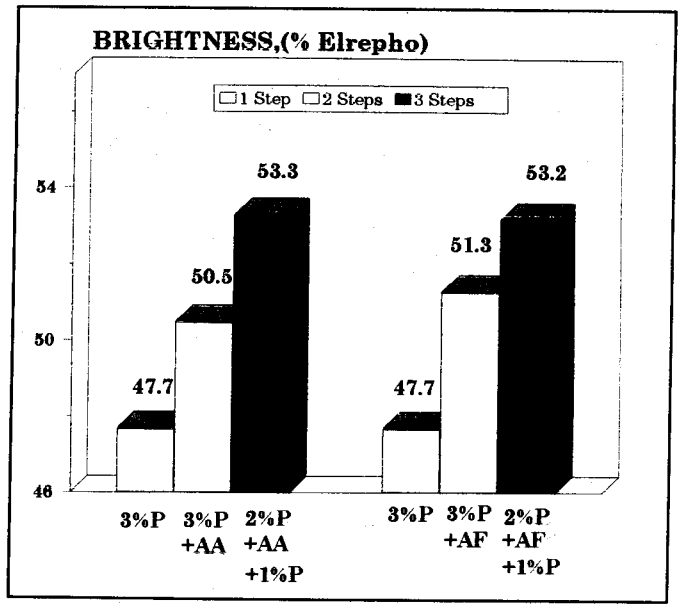


**Fig. 12 Acetic and formic acid treatment influence during bleaching.**

treatment with acetic or formic acids, brightness of 53.3 % Elrepho is obtained if acetic acid is used and 53.2 % Elrepho if the intermediate treatment is with formic acid **(fig.12).**

The treatments with acetic and formic acids are more efficient if they are applied after 2 % peroxide bleaching in the first step, which can be observed in **fig. 13,** such figure shows that formic acid treatment plus 2 % peroxide bleaching gives a brightness value of only 45.6 % Elrepho, but if acetic acid is used, the brightness is 46.5 % Elrepho; inverse treatments, that means, first, bleaching with peroxide and then treating the pulp with formic or acetic acids, values of 48.6 % and 48.5 % Elrepho in brightness are respectively obtained.

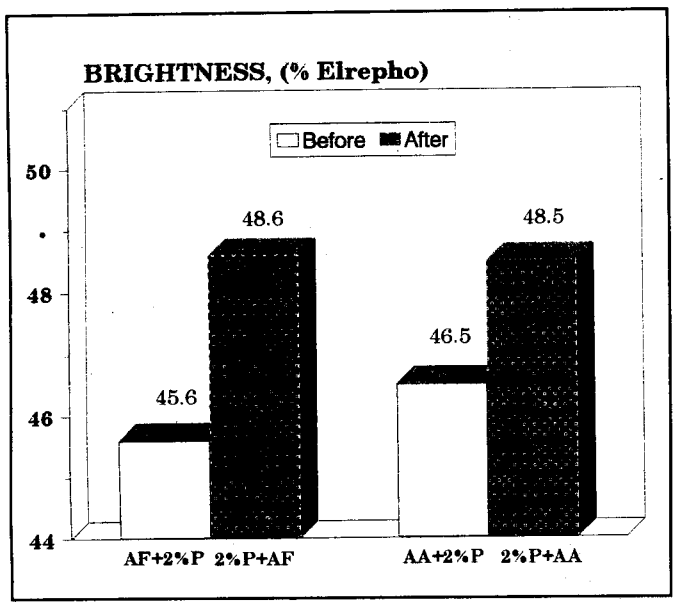


**Fig. 13 Acetic and formic acids treatment influence before and after peroxide teatment.**

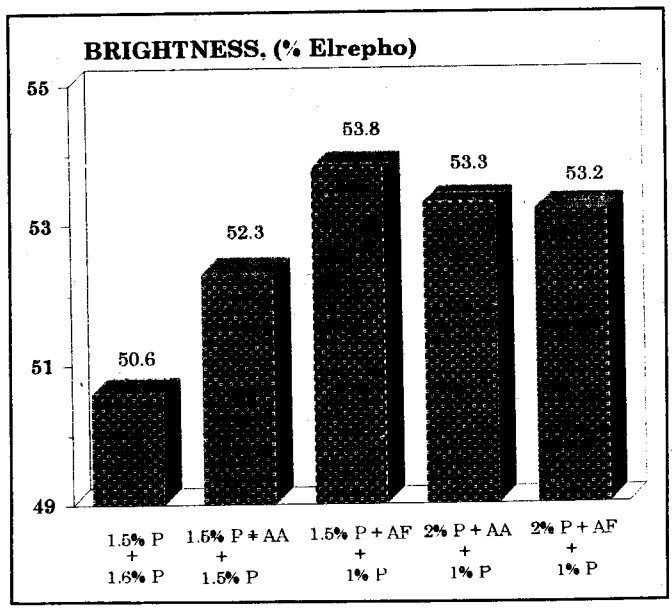


**Fig. 14 Two step peroxide bleaching with and without acetic and formic acids treatment.**

The best bleaching results were obtained when peroxide was distributed in two steps, and with an acetic or formic acid treatment between bleaching steps (fig. 12 and 14), in this way, brightness values

**TABLE I**

**Bleaching conditions and pulp brightness results**

| NUMBER | PEROXIDE (%) | ACETIC A. (%) | FORMIC A. (%) | PEROXIDE (%) | BRIGHTNESS (% ELREPHO) |
|---|---|---|---|---|---|
| 1 | 3.0 | --- | --- | --- | 47.7 |
| 2. | 1.5 | --- | --- | 1.5 | 50.6 |
| 3 | 3.0 | 50 | --- | --- | 50.5 |
| 4 | 3.0 | --- | 50 | --- | 51.3 |
| 5 | 2.0 | 50 | --- | 1.0 | 53.3 |
| 6 | 2.0 | --- | 50 | 1.0 | 53.2 |
| 7 | 2.0 | 50 | --- | --- | 48.5 |
| 8 | 2.0 | --- | 50 | --- | 48.6 |
| 9 | --- | 50 | --- | 2.0 | 46.5 |
| 10 | --- | --- | 50 | 2.0 | 45.6 |
| 11 | 1.5 | 50 | --- | 1.5 | 52.3 |
| 12 | 1.5 | --- | 50 | 1.5 | 53.8 |
| 13 | --- | 10 | --- | 5.0 | 48.7 |
| 14 | --- | 6 | --- | 3.0 | 47.7 |

of 52.3 % and 53.8 % Elrepho respectively, can be obtained. With acetic acid treatment, is better to distribute the peroxide bleaching in two steps, 2 % and 1 %, obtaining a gain of 1 percent more than when peroxide is distributed with a 1.5 % in each step, but, with formic acid treatment, the best distribution seems to be 1.5 % peroxide in each step.

## CONCLUSIONS

The above results indicate that the process with a mixture of acetic acid and water, seems to be interesting for the production of chemimechanical pulps from sugarcane bagasse.

In order to obtain pulps with properties good enough for paper making, a 30 % of acetic acid in the first step and 60 % in the second one were required, and a temperature of 90° C and a pre-treatment time of 2 hours were necessary.

By means of the cooking conditions combination, in the acetic acid and water pulping process, a pulp appropriate for peroxide bleaching was obtained with the following properties: 2.36 Km in breaking length, 2.79 $mNm^2/g$ in tear strength, 32.3 $m^2/Kg$ in light scattering coefficient, and 36.5 % Elrepho in the unbleached pulp brightness.

During the pulp bleaching with hydrogen peroxide, better results are obtained if the peroxide is distributed in two bleaching steps. In this way, with 3 % of hydrogen peroxide a final brightness of 50.6 % Elrepho is obtained. With acetic and formic acid treatments between the bleaching steps, the final brightness is increased at 53.3 % and 53.8 % Elrepho respectively.

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