Pulp and Paper from Blue Agave Waste from Tequila Production

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Pulping of blue agave waste, from the production of tequila, was evaluated by both chemical and biomechanical pulping processes. Two conventional and two organosolv systems were used to pulp the agave waste under a standard set of conditions. The soda−ethanol process was superior in terms of delignification and pulp properties in comparison to the soda and ethanol organosolv processes for pulping of agave waste; however, the kraft process gave the best strength properties. In general, the strength of the agave waste pulps was rather poor in comparison to wood and other agro-based pulps; however, the tear strength was relatively high. This result is typical of poorly bonded sheets and may be due to the coarseness of the agave fibers and/or loss of hemicelluloses in the steaming process for the tequila production. Fungal treatment of the agave waste with *Ceriporiopsis subvermispora* reduced the energy consumption for mechanical refining but gave biomechanical pulps with inferior strength properties. The blue agave chemical pulps should be suitable for blending with softwood kraft pulps for publication grade paper.

Keywords: *Organosolv pulping; kraft pulping; soda pulping; soda−ethanol pulping; biomechanical pulping; nonwood fiber pulp; agave pulp; agave waste; agave paper properties; tequila byproducts*

INTRODUCTION

Blue agave (*Agave tequilana* Weber), a member of the lily family, is grown extensively in the regions east and west of Guadalajara in Central Mexico. It is the raw material for production of the alcoholic beverage tequila. The origin−domination tequila name is applicable only to distillate from Weber blue agave grown within the limits of the State of Jalisco; a minimum content of 51% of blue agave distillate is required to warrant the label of tequila. The tequila name is derived from that of an early native Indian tribe that settled near the present town of Tequila in Jalisco.

Over 1 million blue agave plants cover the hills of the Sierra Madre region of Jalisco (Figure 1). They are planted in rows at ∼1000 per acre. The plants mature in 8−10 years when the sugar content is at a maximum. The agave plant has two main parts: the long spiked leaves from which sisal type fibers can be obtained and the "head" or "piña" (pineapple) from which juices are extracted for alcohol (tequila) production. After the leaves are removed, the head looks like a pineapple, hence, the Spanish name piña (Figure 2). The piña weighs roughly 30−50 kg after removal of the leaves. It is important to note, however, that fibers derived from the leaves are not commercially produced from the blue agave, which is grown exclusively for tequila production. Sisal is derived from the leaves of another species of agave, *Agave sisilana*.

At the distillery, the piñas are split in two, placed in a large kiln, and steamed for ∼11 h in modern stainless steel vessels and for up to 24 h in older brick or stone vessels. After steaming, the piñas are shredded and compressed in roll mills to further expel the solution of hydrolyzed sugars, which is then yeast fermented to the classic tequila beverage. The shredded agave fibrous waste is further washed with water and finally burned or sent to a landfill. It was felt that this waste product could be a valuable source of paper-making fibers, and therefore we have explored various approaches for pulping the blue agave waste.

There are a wide variety of approaches that can be evaluated for pulping of plant materials. We decided to initially explore both conventional and nonconventional pulping methods, which included the conventional kraft and soda processes and the evolving nonconventional organosolv and biomechanical pulping methods. There are a large number of organosolv systems that can be evaluated, but it has been shown in previous work and in our current studies that acid-based organosolv processes, as well as sulfite pulping, are not suitable for agro-based materials (Young, 1997, 1998; Young and Akhtar, 1998; Hergert, 1998). The reasons for the detrimental effects on pulp strength from the acidic systems are not certain but may be related to the different structure of lignin in the agro-based plants (Sarkanen and Hergert, 1971). The two organosolv systems selected for pulping of agave waste were aqueous ethanol and soda−ethanol processes (Hergert, 1998; Martin and Granzow, 1982). Marton and Granzow (1982) found that delignification of spruce proceeded more rapidly and more selectively with soda−ethanol compared to soda alone and in some cases was equivalent to that with kraft pulping. Thus, the use of soda−ethanol resulted in higher yields at a given kappa number, higher brightness than soda and kraft pulps at the same kappa number, and greater bonding potential. However, the improved bonding resulted in lower tear strength for the spruce soda−ethanol pulps.

We have also been exploring biomechanical pulping of agro-based materials for the past five years and have obtained very good results from this approach (Young et al., 1999; Sabharwal, 1998; Sabharwal et al., 1994,

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10.1021/jf990045n CCC: $18.00
Published on Web 09/04/1999

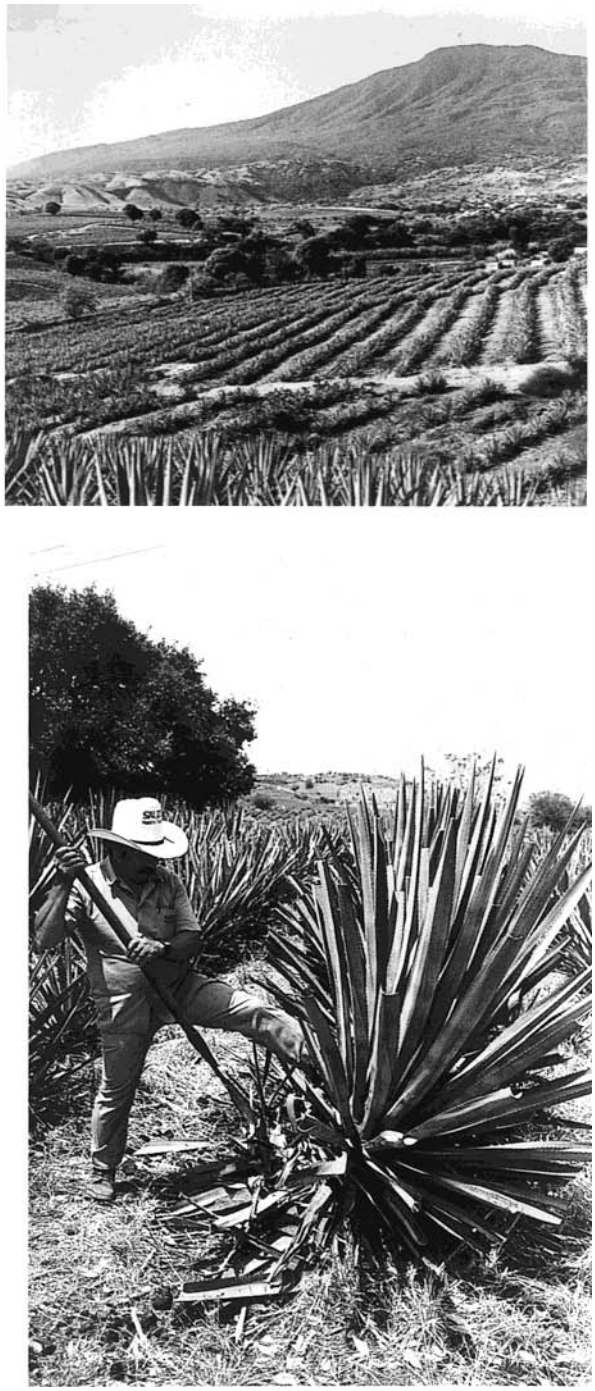

Figure 1. Growth and harvesting of Weber blue agave: (A) large plantation of blue agave in the foothills of the Sierra Madre Mountains of Central Mexico; (B) harvesting of the blue agave plant by a "jimadore", a field hand for agave harvest.

1995). It was felt that evaluation of pulping of agave waste with these five systems would give a good indication of the potential for producing pulp and paper from this material.

EXPERIMENTAL PROCEDURES

Weber blue agave waste (shredded) was obtained from the Jose Cuervo Tequila plant in Tequila, Jalisco, Mexico, and used for the pulping trials without further treatment. The cooks were conducted in 1-L stainless steel pressure vessels immersed in a hot oil bath for control of temperature. The time to maximum temperature was 20−30 min, and the time at maximum temperature (165, 175, and/or 185 °C) was varied from 45 min to 3 h. All cooks were conducted at a 7:1 liquor-to-agave ratio. The conditions for the kraft cook were 20% active alkali and 25% sulfidity. The ethanol organosolv cook was conducted with 50% aqueous ethanol (v/v), the soda cook at 20% sodium hydroxide concentration (based on charge of agave, oven-dry basis), and the soda−ethanol cook at 20% sodium hydroxide concentration (based on charge of agave, oven-dry basis) in 50% aqueous ethanol (v/v). The pulps were beaten in a laboratory PFI mill to ∼300 mL Canadian Standard freeness. Tappi standard methods were utilized for measurement of kappa number, sheet preparation, and all strength evaluations. Brightness is expressed as percent ISO.

Figure 2. Split heads or piñas of blue agave after the leaves have been removed ready for packing into the steaming ovens.

Table 1. Comparative Properties of Pulps from Agave Waste[a]

	kraft	ethanol	soda	soda−ethanol
yield, %	40.7	51.3	57.9	51.6
kappa no.	28	58	60	33
freeness	317	295	333	295
tensile index, Nm/g	25.09	23.98	27.9	26.38
burst index, kPa·m^2/g	1.2	1.01	1.47	1.27
tear index, mN·m^2/g	9.39	5.31	7.35	6.76
brightness, %	19.4	16.1	14	16.5

[a] All cooks were run at 175 °C for 2 h. Yield vs time at differents temperatures (soda cooking); kappa number vs time at different temperatures (soda cooking).

RESULTS AND DISCUSSION

Comparative Evaluation by Chemical Pulping. Table 1 shows the characteristics of the pulps obtained from the four chemical pulping processes. Standard conditions were utilized to obtain kraft and ethanol organosolv pulps, whereas soda and soda−ethanol organosolv pulpings were explored in greater detail. We selected, as a standard for comparison, pulping at a maximum temperature 175 °C for 2 h. Higher yields were obtained for the soda and organosolv pulps under similar pulping conditions compared to kraft pulping (Table 1). Under the standard conditions, the kappa numbers for kraft and soda−ethanol pulps were very similar (kappa no. 28 versus 33), whereas the soda and ethanol pulps had much higher kappa numbers (kappa no. 60 and 58). We evaluated a series of different pulping conditions to reduce the kappa number of the ethanol pulps, which were not successful; therefore, only the one best condition is reported in Table 1.

In general, the strength of the agave chemical pulps was rather poor. The burst index and tensile strength of the pulps were comparable under the selected pulping conditions (Table 1). The tear strengths, however,

Table 2. Pulping Conditions and Properties of Soda and Soda−Ethanol Agave Pulps

reaction temp, °C	time, min	yield, %	freeness	kappa no.	tensile index, Nm/g	tear index, mN·m²/g	burst index, kPa·m²/g	brightness, %
				Soda Cooking				
175	45	56.7	315	71	22.50	7.87	1.24	17.1
175	60	55.0	327	74	18.26	5.97	0.91	16.0
175	120	57.9	333	60	27.90	7.35	1.47	14.0
175	180	58.1	320	67	23.42	8.80	1.17	13.6
185	45	54.0	318	66	22.02	7.40	1.12	15.3
185	60	53.4	298	64	27.28	7.58	1.35	14.6
185	120	49.2	289	59	26.28	7.47	1.40	12.9
185	180	46.2	302	58	21.56	7.62	1.20	11.5
				Soda−Ethanol Cooking				
165	45	57.3	308	38	25.61	7.33	1.22	22.0
165	60	47.9	311	31	24.27	7.27	1.25	22.2
165	120	49.6	326	28	25.13	7.29	1.28	22.3
175	45	51.8	321	30	23.59	7.30	1.29	20.5
175	60	50.0	322	26	24.75	7.23	1.33	21.1
175	120	51.6	295	33	26.38	6.76	1.27	16.5
185	45	50.1	315	30	23.67	7.26	1.25	19.0
185	60	50.2	329	31	25.38	7.79	1.34	18.2
185	120	51.6	332	32	25.91	6.36	1.25	16.4

showed significant differences for the pulps. The kraft pulp typically exhibited the highest tear strength, which was 20% greater than the tear strength of the soda and soda−ethanol pulps. The tear strength was relatively high compared to the low tensile and burst strengths exhibited by the agave pulps. However, the tear strength of the ethanol pulp was >40% less than that of the kraft pulp.

The highest brightness was found for the kraft pulp at 19.4 (Table 1); however, in further pulping trials, described below, a brightness higher than that of kraft pulp was obtained for the soda−ethanol pulps (22). The lowest brightness was exhibited by the soda and ethanol pulps. The difference in this case is probably due to the higher kappa number of the unbleached soda and ethanol pulps compared to the kappa number of the kraft pulp, which would be expected to give lower brightness.

On the basis of this preliminary investigation it was decided to further explore the soda and the soda−ethanol processes for pulping of agave waste. Kraft pulping appears to be suitable for the agave waste because, under the standard conditions, it gave a pulp with a low kappa number and the best overall strength properties. However, we wanted to further explore non-sulfur systems that would be more environmentally benign and which could potentially give pulp properties equivalent to those for the kraft agave waste pulps.

Soda and Soda−Ethanol Organosolv Pulpings of Agave Waste. The pulping conditions and pulp properties for the additional trials for pulping of agave waste by the soda and soda−ethanol processes are also shown in Table 2. Four different times and two different temperatures were selected for soda pulping with a 20% sodium hydroxide solution, and one additional temperature was chosen for pulping with the soda−ethanol process. Figures 3 and 4 show the effect of temperature and time on the kappa number of soda and soda−ethanol pulps, respectively, from agave waste. At 175 °C, the lowest kappa number is achieved after 2 h of pulping in the soda system, and then it appears to increase, possibly due to condensation reactions (Young, 1998). At the highest temperature (185 °C) the kappa number is reduced more rapidly but the delignification is equivalent at both temperatures after 2 h of cooking time. As shown in Figure 4, the lowest kappa number

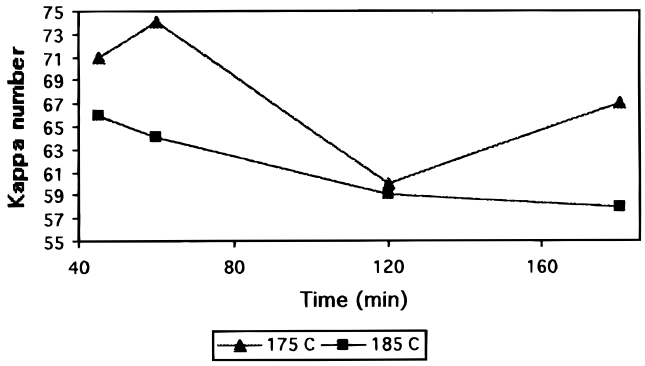

Figure 3. Kappa number vs time of cooking at different temperatures for soda pulping of blue agave waste.

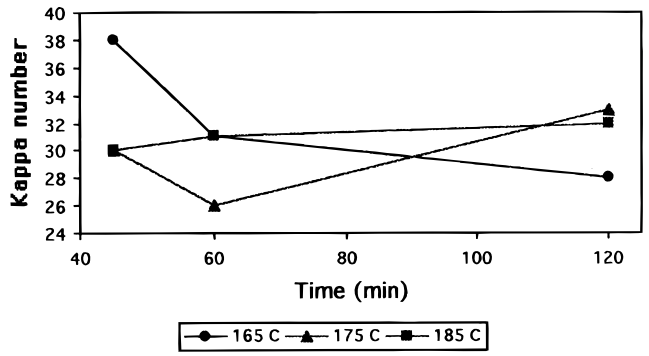

Figure 4. Kappa number vs time of cooking at different temperatures for soda−ethanol pulping of blue agave waste.

for soda−ethanol pulps was obtained after 1 h of cooking at 175 °C; cooking at the higher temperature (185 °C) did not offer any advantage in terms of delignification.

The effect of time and temperature on pulp yield from soda and soda−ethanol cooks is shown in Figures 5 and 6. As shown in Figure 5, the pulp yield is substantially higher for the 2-h soda cooks when the maximum temperature is 175 versus 185 °C. Because the pulp kappa numbers are approximaely the same under these conditions, it would be advantageous to operate at the lower temperature for more complete utilization of the plant material. The soda−ethanol process gives the lowest yield for the cooks at the lowest temperature (165 °C), which appears to be an anomaly (Figure 6). The yields for cooking at 175 and 185 °C are essentially the

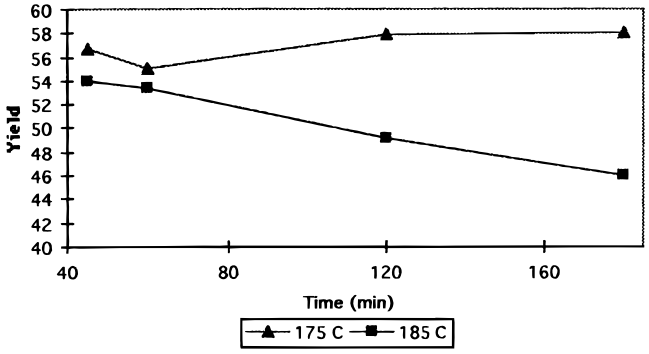

Figure 5. Percent yield vs time of cooking at different temperatures for soda pulping of blue agave waste.

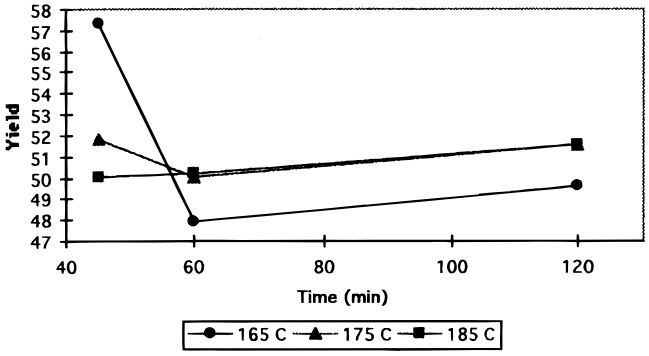

Figure 6. Percent yield vs time of cooking at different temperatures for soda–ethanol pulping of blue agave waste.

same; therefore, cooking at 175 °C would be desirable because this also gives the greatest amount of delignification.

The soda and soda–ethanol pulp properties are shown in Table 2 as a function of cooking time at various temperatures. There does not appear to be any advantage for improvement of burst strength by cooking at the higher temperature (185 °C) after 2 h. It is not clear why the burst strength is low after cooking for 1 h at 175 °C. However, the optimum cooking time for maximum burst strength for the soda–ethanol pulps is clearly 1 h. Cooking at higher temperature (185 °C) offers no advantage over cooking at 175 °C for maximum burst strength.

The pulp tensile strength shows behavior almost identical to that of the burst strength in response to changes in cooking time and temperature for the soda pulps. The maximum tensile strength is obtained at 1 h of cooking at either 175 or 185 °C. However, the tensile strength continues to rise with increased cooking time for the soda–ethanol pulps. The maximum tensile strength was obtained at 2 h of cooking at 175 °C.

The maximum tear strength for the soda pulp is obtained after 3 h of cooking at 175 °C, whereas at 2 h of cooking the tear strength is essentially the same for cookings at both 175 and 185 °C. The prolonged cooking at high temperature may be detrimental to individual fiber strength in the soda process. Prolonged cooking at higher temperatures was also found to be detrimental to tear strength for soda–ethanol pulps. However, the highest temperature (185 °C) was found to give the maximum tear strength after 1 h of cooking in the soda–ethanol liquor. Clearly the addition of ethanol to the soda cooks (soda–ethanol pulping) alters that delignification behavior and the strength properties.

The effects of temperature and time of cooking on the brightness of soda and soda–ethanol pulps are shown in Table 2. Prolonged cooking at high temperature (185 °C) has a negative effect on the brightness of soda pulps. There was a distinct brightness advantage when soda–ethanol liquors were used; brightness in the range of 19–22.3 could be obtained at the three different temperatures for cooking times of 1 h or less. However, after 2 h of cooking at 175 and 185 °C the brightness dropped to ~16.5.

Table 3. Biomechanical Pulping of Agave Waste[a]

treatment	energy consumption, kW·h/ton	tensile index, Nm/g	tear index, mN·m²/g
control	503	6.86	1.29
biotreated, 2 weeks	347	5.25	1.05
biotreated, 3 weeks	333	2.89	0.82

[a] Biotreatment with *C. subvermispora*.

The soda–ethanol process appears to be superior in terms of delignification and pulp properties in comparison to the soda and ethanol organosolv processes for pulping of blue agave waste; however, the kraft process gives the best strength properties. In general, the strength of all the agave waste pulps was rather poor, although the tear strength was relatively high. This may reflect poorly bonding fibers in the paper, which would be expected to have low tensile and burst strengths and relatively higher tear strength. The agave fibers were rather coarse, which would reduce the bonding and improve the tear strength. It is also probable that the hemicelluloses were extensively modified and/or removed in the steaming process to extract the sugars for alcohol fermentation. The loss of the hemicelluloses would reduce the bonding potential, and this would explain the low burst and tensile strengths and the relatively higher tear strength. Further work is underway to ascertain the chemical and physical properties of the agave fibers to verify these postulations.

Biomechanical Pulping of Agave Waste. Another alternative for pulping of wood and agro-based materials is biomechanical pulping. Biomechanical pulping involves the deliberate harnessing of white-rot fungi to degrade and/or modify lignin and render the plant material more susceptible to mechanical disintegration, with concomitant improvement in strength properties, compared to conventional mechanical pulps (Young and Akhtar, 1998; Akhtar et al., 1998). This process has been extensively evaluated for production of pulps from wood and is near commercialization for conversion of wood chips into biomechanical pulps. In recent years we have evaluated biomechanical pulping for a variety of agro-based materials and have found it to give even better results with the annual type plants (Sabharwal et al., 1994, 1995; Bustamante, 1999; Young et al., 1999). Agro-based materials generally have lower lignin contents and are more amenable to treatment with the fungi.

We utilized the same white-rot fungi, *Ceriporiopsis subvermispora*, for treatment of agave waste, as was found to give superior behavior with both wood and several agro-based materials. Table 3 shows the energy consumption for mechanical disintegration (refiner mechanical pulping) of agave and fungal-treated agave. It is clear that there is a substantial reduction in energy consumption with refining after 2 and weeks of fungal treatment of the agave waste, similar to what was found for other agro-based plant material (Sabharwal et al., 1994, 1995; Bustamante, 1999; Young et al., 1999).

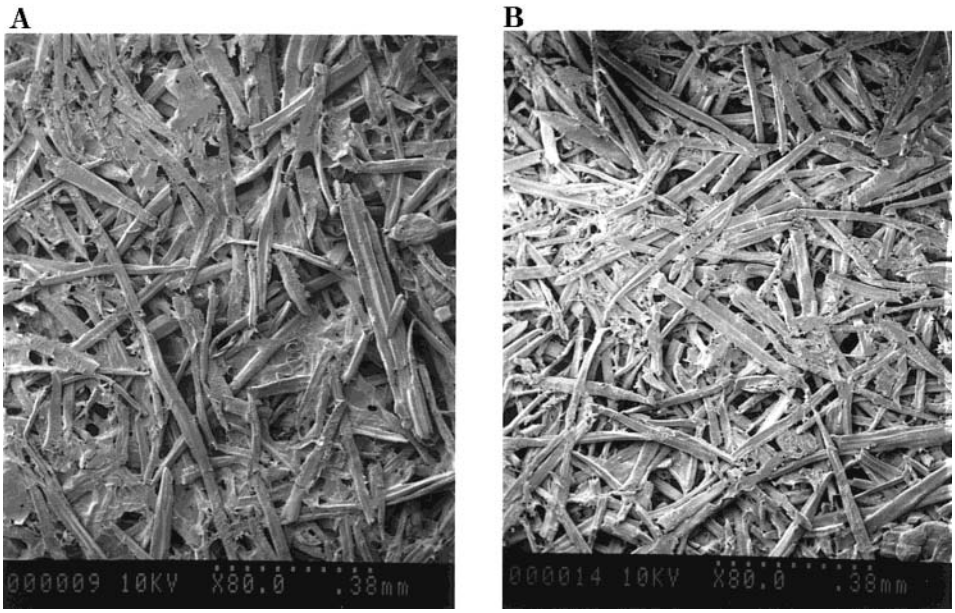

Figure 7. Scanning electron micrographs (×80) of (A) conventional mechanical agave waste pulp fibers and (B) biomechanical agave waste pulp fibers. Figure is reproduced here at 67% of the original.

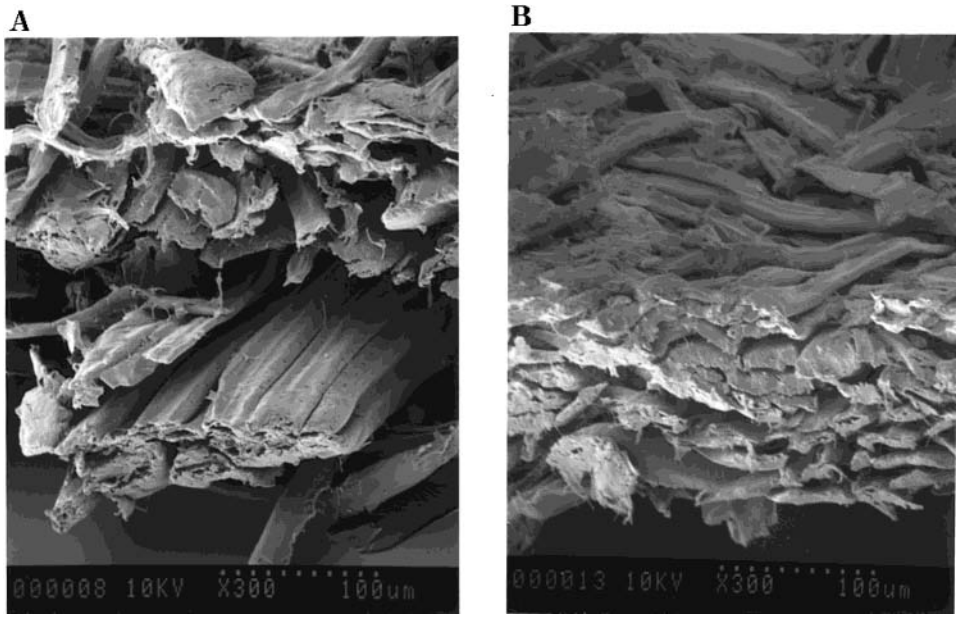

Figure 8. Scanning electron micrographs (×300) of (A) conventional mechanical agave waste pulp fibers and (B) biomechanical agave waste pulp fibers. Figure is reproduced here at 67% of the original.

However, to our surprise, we found no improvement in the strength properties with the fungal treatments prior to mechanical disintegration as shown in Table 3. The biotreatment of agave waste resulted in substantially reduced burst, tensile, and tear strengths.

Scanning electron micrographs at two magnifications were obtained for the conventional mechanical and biomechanical pulps from agave waste to attempt to ascertain why the biomechanical pulps exhibited inferior strength properties (Figures 7 and 8). For both pulps, the fibers appear to be rather short with considerable breakage and other damage. Better fiber separation, with fewer fiber clumps and shives, has been noted for other biomechanical pulps compared to conventional mechanical pulps and is generally indicative of improved strength properties due to better stress distribution in the final sheets (d'A Clark, 1985). This was not the case for the biomechanical pulps from the agave waste. The agave waste is for some reason not amenable to biological treatments with this particular fungus, which demonstrates that each different type of plant material requires detailed investigations to find the optimum conditions for producing quality pulps. The factors postulated for the low strength of the chemical agave pulps may also affect the biomechanical pulps, namely, coarse fibers with reduced hemicellulose composition, which reduces fiber-to-fiber bonding and thus strength properties. The changes in fiber characteristics also negatively impacts tear strength for the biomechanical pulps.

Conclusions. The potential for production of pulp and paper from blue agave waste was demonstrated in this work. The soda−ethanol process was superior in terms of delignification and pulp properties in comparison to the soda and ethanol organosolv processes for pulping of agave waste; however, the kraft process gave

the best strength properties. In general, the strength of all the agave waste pulps was rather poor. However, the paper from the agave waste chemical pulps exhibited relatively high tear strength relative to the tensile and burst strengths, which indicates poorly bonded fibers. It was postulated that the low bonding potential of the agave fibers may be due to their coarse nature and/or reduced quantities of hemicelluloses as a result of the steaming process used for tequila production. Fungal treatment of the agave waste with *C. subvermispora* reduced the energy consumption for mechanical refining but gave biomechanical pulps with inferior strength properties

LITERATURE CITED

Akhtar, M.; Blanchette, R.; Myers, G.; Kirk, T. An overview of biomechanical pulping research. In *Environmentally Friendly Technologies for the Pulp and Paper Industry*; Young, R. A., Akhtar, M., Eds.; Wiley: New York, 1998; pp 273−308.

Bustamante, P.; Ramos, J.; Zuñiga, V.; Sabharwal, H.; Young, R. A. Biomechanical pulping of bagasse with the white rot fungi *Ceriporiopsis subvermispora* and *Pleurotus ostreatus*. *Tappi* **1999**, *82* (6), 123−128.

d'A Clark, J. *Pulp Technology and Treatment of Paper*, 2nd ed.; Miller Freeman: San Franciso, CA, 1985; pp 160−183.

Hergert, H. L. Developments in oganosolv pulping-An overview. In *Environmentally Friendly Technologies for the Pulp and Paper Industry*; Young, R. A., Akhtar, M., Eds.; Wiley: New York, 1998; pp 5−68.

Marton, R.; Granzow, S. Ethanol-alkali pulping. *Tappi* **1982**, *65* (6), 103−106.

Sabharwal, H. Biological approach for pulping and bleaching of nonwoody plants. In *Environmentally Friendly Technologies for the Pulp and Paper Industry*; Young, R. A., Akhtar, M., Eds.; Wiley: New York, 1998; pp 449−480.

Sabharwal, H.; Akhtar, M.; Blanchette, R.; Young, R. A. Biomechanical pulping of kenaf. *Tappi* **1994**, *77* (12), 105−112.

Sabharwal, H.; Akhtar, M.; Blanchette, R.; Young, R. A. Refiner mechanical and biomechanical pulping of jute. *Holzforschung* **1995**, *49* (6), 537−544.

Sarkanen, K.; Hergert. H. Classification and distribution. In *Lignins, Occurrence, Formation, Structure and Reactions*; Sarkanen, K., Ludwig, C., Eds.; Wiley-Interscience: New York, 1971; pp 43−94.

Young, R. A. Processing of agro-based resources into pulp and paper. In *Paper and Composites from Agro-Based Resources*; Rowell, R., Young, R. A., Eds.; CRC-Lewis: New York, 1997; pp 137−245.

Young, R. A. Acetic acid-based pulping. In *Environmentally Friendly Technologies for the Pulp and Paper Industry*; Young, R. A., Akhtar, M., Eds.; Wiley: New York, 1998; pp 133−156.

Young, R. A., Akhtar, M., Eds. *Environmentally Friendly Technologies for the Pulp and Paper Industry*; Wiley: New York, 1998; 577 pp.

Young, R. A.; Bustamante, P.; Ramos, J.; Zuñiga, V.; Sabharwal, H.; Akhtar, M.; Biomechanical pulping of kenaf and other agro-based materials. In *Kenaf: Properties, Processing and Products*; Sellers, T., Ed.; Mississippi State University Press: Mississippi State, MS, 1999.

Received for review January 19, 1999. Revised manuscript received June 25, 1999. Accepted July 19, 1999.

JF990045N