

Carboxymethylcellulose Obtained by Ethanol/Water Organosolv Process Under Acid Conditions

DENISE S. RUZENE,¹ ADILSON R. GONÇALVES,^{*,1}
JOSÉ A. TEIXEIRA,² AND MARIA T. PESSOA DE AMORIM³

¹Departamento de Biotecnologia, Escola de Engenharia de Lorena-USP, CxPostal 116, CEP 12.600-970 Lorena-SP, Brazil; E-mail:adilson@debiq.faequil.br; ²Centre for Biological Engineering, Universidade do Minho, Campus de Gualtar, 4710-057, Braga, Portugal; and ³Centro de Engenharia Têxtil, Universidade do Minho, Campus de Azurém, Portugal

Abstract

Sugar cane bagasse pulps were obtained by ethanol/water organosolv process under acid and alkaline conditions. The best condition of acid pulping for the sugarcane bagasse was 0.02 mol/L sulfuric acid at 160°C, for 1 h, whereas the best condition for alkaline pulping was 5% sodium hydroxide (base pulp) at 160°C, for 3 h. For the residual lignin removal, the acid and alkaline pulps were submitted to a chemical bleaching using sodium chlorite. Pulps under acid and alkaline conditions bleached with sodium chlorite presented viscosities of 3.6 and 7.8 mPa.s, respectively, and μ -kappa numbers of 1.1 and 2.4, respectively. The pulp under acid condition, bleached with sodium chlorite was used to obtain carboxymethylcellulose (CMC). CMC yield was 35% (pulp based), showing mass gain after the carboxymethylation reaction corresponding to 23.6% of substitution or 0.70 groups $-\text{CH}_2\text{COONa}$ per unit of glucose residue. The infrared spectra showed the CMC characteristic bands and by the infrared technique it was possible to obtain a substitution degree (0.63), similar to the substitution degree calculated by mass gain (0.70).

Index Entries: Acid and alkaline catalyzed ethanol pulping; carboxymethylcellulose; chemical bleaching; infrared spectra; sugarcane bagasse; Organosolv pulping.

Introduction

Currently, there is a great interest in using renewable resources for obtaining of industrial products, specially those obtained from residues. Sugar cane bagasse is an agricultural waste abundant in several countries. Brazil has many sugar cane plantations, mainly for the manufacture of sugar and ethanol, which is used as fuel for automobiles. The production of sugar cane bagasse for the year 2004/2005 was 56×10^6 t. About 90% of

*Author to whom all correspondence and reprint requests should be addressed.

this biomass was burned to generate energy for the ethanol distillation and the remaining 10% constitutes a surplus corresponding to 5×10^6 t that could be used for the production of other chemicals and materials, such as cellulose derivatives (1).

Alternative pulping processes utilizing aqueous organic solvents, known as Organosolv, have been extensively studied in the last 30 yr as an alternative to conventional chemical processes of pulping (2–7). These processes can collaborate largely with the decreased environmental impact caused by conventional delignification processes, besides allowing for the integral use of lignocellulosic components in chemical products of commercial interest (3,8,9). Organosolv pulping has been proposed as a promising alternative to chemical pulping. The ethanol/water process combines high efficiency, low cost, and ethanol abundance in countries where sugar cane is economically important (3,10,11). Organosolv pulping methods can be divided into two great groups: (a) acid-catalyzed processes (3), often operated without the addition of an acid catalyst; in such cases, acetic acid released during the pulping process provides the needed acidity (3,12–14) and (b) alkaline organosolv processes, commonly using delignification agents such as NaOH or Na_2SO_3 ; the role of the organic solvent is to promote the solubilization of lignin (3).

Cellulose is a linear and high-molecular weight polymer as well as natural, renewable, and biodegradable material (15). However, because of its inter- and intramolecular hydrogen bonds, cellulose is not dissolved by common solvents (16). In order to utilize cellulose industrially, cellulose must be converted to soluble derivatives. Cellulose derivatives have gained acceptance for pharmaceutical, cosmetic, food, adhesives, textiles, and packaging uses. They must be nontoxic, noncarcinogenic, biocompatible, and nonharmful to the biological environment. Cellulose ether is the most widely used cellulose derivative in food and pharmaceutical industries. Conversion of cellulose to sodium carboxymethylcellulose (CMC), an anionic linear cellulose ether, is another example.

CMC is an important industrial polymer with a wide range of applications in detergents, textiles, paper, drag reduction, foods, drugs, and oil. It is prepared by treating cellulose with aqueous sodium hydroxide followed by reaction with chloroacetic acid. Sodium carboxymethyl groups ($-\text{CH}_2\text{COONa}$) are introduced into the cellulose molecule, which promote water solubility (17,18). The various properties of CMC depend on three factors: molecular weight of the polymer, average carboxyl content per anhydroglucose unit, and the distribution of carboxyl substituents along the polymer chains (19). The CMC structure is based on the $\beta(1 \rightarrow 4)$ -D-glucopyranose polymer of cellulose. Different preparations may have different degrees of substitution, but are generally in the range 0.6–0.95 carboxymethyl groups per monomer units (20). The structure of CMC is shown in Fig. 1. The objective of this work was to produce CMC from an ethanol/water organosolv lignocellulosic process under acid conditions.

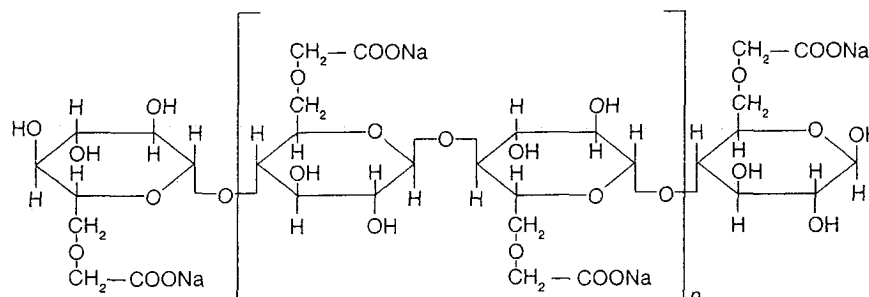


Fig. 1. Sodium CMC molecule structure.

Materials and Methods

Pulping and Bleaching

Pulping of depithed sugar cane bagasse with ethanol/water 1 : 1 (v/v) mixture was carried out in a closed and pressurized vessel (gram bagasse, liquor to bagasse ratio). The pulping was conducted using H_2SO_4 in the concentration range of 0.01–0.05 mol/L for 0.5–2 h and NaOH (5–10% dry bagasse) for 3 h. The products were filtered and the pulp was dried for yield determination. Dried and refined pulps (10 g) were suspended in 333 mL of water (3% consistency) and heated to $70 \pm 5^\circ\text{C}$. Sodium chlorite (8.4 g) and glacial acetic acid (3.4 mL) were added. The solution was further heated to $70 \pm 5^\circ\text{C}$ for 60 min. Afterward, the samples were cooled in ice bath to 10°C . Bleached pulp was filtered, washed with water (3 L), and dried (21).

Analysis and Chemical Composition of the Pulps

Kappa-number and viscosities of the pulps were determined by standard methods (22,23). One gram of dry pulp was treated with 10 mL of 72% H_2SO_4 with stirring at 45°C for 7 min. The reaction was interrupted by adding 50 mL of distilled water, and the mixture was then transferred to a 500-mL Erlenmeyer flask, and the volume brought to 275 mL. The flask was autoclaved for 30 min at 1.05 bar for the complete hydrolysis of oligomers. The mixture was filtered and the hydrolysate brought to 500 mL. A sample (40 mL) of the hydrolysate was diluted to 50 mL and the pH was adjusted to 2.0 with 2 mol/L of NaOH. After filtration through a Sep-Pak C_{18} cartridge (Waters, Milford, MA) to remove aromatic compounds, the hydrolysate was analyzed in an Aminex HPX-87H column ($300 \times 7.8 \text{ mm}^2$) (Bio-Rad Laboratories Ltd., Hercules, CA) at 45°C using a Shimadzu chromatograph LC-10AD (Shimadzu Co., Tokyo, Japan) with refractive-index detector. The mobile phase was 0.005 mol/L H_2SO_4 at 0.6 mL/min flow rate. Sugar concentrations, reported as xylan and glucan, were determined from calibration curves of pure compounds. Lignin was determined by gravimetric analysis (24).

Determination of Brightness

The brightness of pulps was determined in agreement with Technical Association of the Pulp and Paper Industry (TAPPI) (25). Samples were prepared following the TAPPI norm (26): 3 g of pulp (dry base) were disaggregated by 5 min at pH 5.5 and 0.3% consistency. The pulp suspension was filtered in Büchner funnel (110-mm diameter). After filtration, the funnel was inverted and pulp was liberated using airflow. The formed leaf was pressed (10–12 kgf/cm²) for 90 s and dried in the dark. After 1 d, the sheets with thickness between 310 and 315 g/m² were analyzed using Photovolt 577 equipment (Photovolt Instruments Minneapolis, MN). The reflection percentage was determined at five different points and the results were presented as average values.

Determination of Holocellulose

Five-gram samples of dry pulp (with known moisture) were transferred to 250-mL Erlenmeyer flasks with 160 mL of distilled water, 0.5 mL of acetic acid, and 1.5 g of sodium chlorite. The samples were heated in water bath at 70–80°C with agitation every 10 min for 60 min. Then, 0.5 mL of acetic acid and 1.5 g of sodium chlorite were added. This addition was repeated at 60 min intervals for 4-h reaction time. After 4 h the Erlenmeyer flask was put in ice bath and cooled to 10°C, then the samples were filtered in crucibles of porosity 2. The residue was washed with 1.6 L of hot distilled water under suction. Subsequently, samples were washed with acetone and dried at room temperature (21).

Determination of α -Cellulose

One-gram samples of holocellulose (with known humidity) were transferred to 150-mL beakers and put in water bath at 20°C. Then, 11.8 mL of 17.5% NaOH solution were added with stirring, 5 mL being added in the first 1 min, 3.4 mL in the next 45 s, and 3.4 mL in the next 15 s. The samples were left at rest by 3 min and then 13.6 mL of 17.5% NaOH was added over 10 min, 3.4 mL with stirring initially, 3.4 mL were added in the 2.5th min, 3.4 mL in the 5th min, and 3.4 mL in the 7.5th min. Samples were covered and left in for 30 min at 20°C. Afterwards, 33.4 mL of distilled water was added, and the mixture was left for another 30 min at 20°C. The samples were filtered in crucible of porosity 2, washed with 8 mL of 8.3% NaOH, and washed with 400 mL of distilled water. The volume was completed with acetic acid 2 mol/L and left at rest for 3 min. The samples were filtered to remove acetic acid, washed with 3 L of distilled water to room temperature and dried overnight (21).

Synthesis of Sodium CMC

A sample of 5 g bleached pulp was transferred to 500-mL two-necked flask with 92.5 g ethanol and 3.7 g water. A solution of sodium hydroxide (5 g

of NaOH and 8 g of water) was added in the mixture, within the addition time of 30 min, under mechanical agitation and put in water bath at $15 \pm 5^\circ\text{C}$. On completion of the addition, the mixture was agitated for 1 h, maintained in the water bath at $15\text{--}25^\circ\text{C}$. After the alkalization, a solution of monochloroacetic acid and ethanol to 50% of the mass (6.5 g of monochloroacetic acid and 6.5 g of ethanol) was added in the reactional mixture with 30 min addition time, mechanical agitation, and water bath at $20 \pm 5^\circ\text{C}$. At the end of the addition, the sample was heated at 60°C and agitated for 3 h. Afterward, the mixture was drained and the solid phase suspended in 70% methanol and neutralized while in suspension with 90% acetic acid. The suspension was filtered, and the precipitate washed repeatedly with ethanol, methanol, and dried at $60 \pm 5^\circ\text{C}$. The mass gain of CMC was determined by the Eq. 1 (27).

$$\text{MG}(\%) = \frac{\text{CMCM} - \text{Mbp}}{\text{Mbp}} \times 100 \quad (1)$$

where MG (%) is the mass gain of the CMC, CMCM is the CMC mass (gram dry base), and Mbp is the mass of bleached pulp (gram dry base).

Fourier Transform Infrared of CMC

Fourier-transform infrared (FTIR) spectra were obtained directly from sample of CMC utilizing the high attenuated total reflectance technique in Nicolet Avatar 360 FTIR spectrometer (Nicollet Instrument Corporation, Madison, WI).

Results and Discussion

The composition of sugar cane bagasse pulps is given in Table 1. Yield values (using refined pulps) were 19% greater for the pulp under alkaline treatment. Viscosity values were 53% lower for the acid treatment because of higher degradation of fibers, in other words, the degree of polymerization of cellulose decreased. The kappa-number remained around 40, indicating that residual lignin still remained in the pulp. The amount of glucan was 27% higher for the acid treatment in respect to the total amount evaluated. Values for xylan and total lignin were 90.1 and 33.6% higher for the alkaline treatment. The holocellulose values were around 90%. Values for α -cellulose were 70%, whereas the brightness for acid and alkaline conditions was of 30.5 ± 1.2 and $25.0 \pm 1.2\%$, respectively. Faria (28) found brightness of 35.4% for NaOH pulps of bagasse, indicating that the results were close to those reported in the literature (29).

Table 2 gives the composition of bleached pulps. The classified yield values of the bleached pulps were higher than 89%. Viscosity was preserved after chemical bleaching and fiber degradation did not occur. In general, the reagents used in the bleaching sequence partially removed the lignin, without reducing the viscosity. The kappa-number was reduced significantly showing

Table 1
Chemical Composition and Analysis of Sugar cane Bagasse Pulps

	Puping conditions	
	Acid ^a	Alkaline ^b
Classified yield (%)	33.1	40.9
Viscosity (mPa·s)	3.8 ± 0.2	8.1 ± 0.2
Kappa-number	41.1 ± 0.4	46.2 ± 0.6
Glucan (%)	75.9 ± 3.2	55.3 ± 0.6
Xylan (%)	2.2 ± 0.1	23.1 ± 0.5
Klason lignin (%)	9.7 ± 0.3	14.6 ± 0.9
Holocellulose (%)	91.2 ± 0.1	89.1 ± 1.1
α-Cellulose (%)	70.4 ± 0.9	68.4 ± 0.3
Brightness	30.5 ± 1.2	25.1 ± 1.2

^aAcid (0.02 mol/L H₂SO₄), 1 h at 160°C.

^bAlkaline (5% NaOH), 3 h at 160°C.

Table 2
Chemical Composition and Analysis of Bleached Pulps

	Bleached pulp	
	Acid condition ^a	Alkaline condition ^b
Classified yield (%)	92.6	89.7
Viscosity (mPa·s)	3.6	7.8
Kappa-number	1.1 ^c	2.4 ^c
Glucan (%)	69.5	64.6
Xylan (%)	2.3	21.9
Klason lignin (%)	1.8	6.2
Holocellulose (%)	98.4	98.1
α-cellulose (%)	69.8	69.4
Brightness	82.3 ± 0.8	68.3 ± 1.6

^aAcid (0.02 mol/L H₂SO₄), 1 h at 160°C.

^bAlkaline (5% NaOH), 3 h at 160°C.

^cμ-κ number.

after bleaching a μ-kappa value of 1.1 (acid condition) or 2.4 (alkaline condition), indicating that the residual lignin of the pulp was practically removed. The glucan and xylan were preserved after bleaching. The total lignin was also reduced with the bleaching. Values of α-cellulose were not changed indicating no reduction in the polymerization degree of the cellulose. The brightness was elevated to 63% for the two bleaching conditions showing that with the removal of the residual lignin the value for brightness increased.

In contrast, with the pulps used for papermaking, both xylan and lignin are undesirable and should be removed during the pulping and

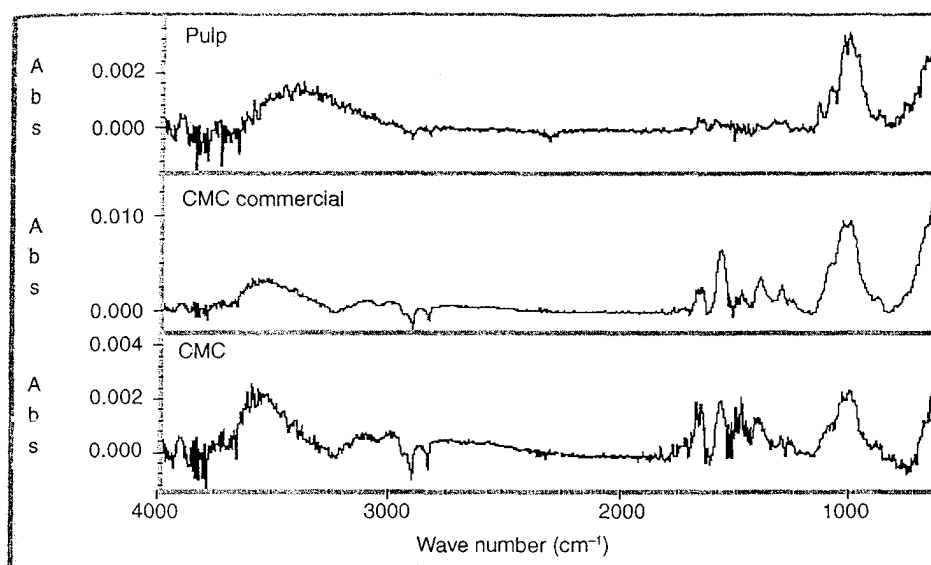


Fig. 2. FTIR spectra of the pulp in acid condition bleached with sodium chlorite, CMC commercial, and CMC obtained in this article.

bleaching sequences (30). The pulp used for CMC production was the ethanol/water/ H_2SO_4 (acid condition) pulp. This pulp presented the best conditions of κ -number, brightness and smaller amount of xylan.

Carboxymethylcellulose

Figure 2 shows the FTIR spectra of the ethanol/water/acid organosolv pulp bleached with sodium chlorite, commercial CMC, and of CMC obtained in this work. The carboxymethylation reaction occurs through the substitution of one hydrogen atom of the group hydroxyl for a carboxymethyl group. A decrease in the absorbance of the band in the region related to the axial stretching of O–H at 3600 cm^{-1} and a displacement of this band in the region around $3650\text{--}3700\text{ cm}^{-1}$ were observed.

The decrease of the absorbance is because of the etherification of the cellulose O–H groups for carboxymethylic groups and the displacement to the decrease of the intramolecular hydrogen bonds. Another evidence is observed in the region of $1150\text{--}1000\text{ cm}^{-1}$, in which the bands occur as a result of the C–O and C–O–C links, typical of ethers. The introduction of the CH_2COONa group in the cellulose structure (this group possesses the carbonyl bond inserted in the carboxylate group) absorbs in the $1650\text{--}1550\text{ cm}^{-1}$ range because of the asymmetrical axial deformation. This band differentiates the spectrum of the cellulose from that of CMC. Acid pulp bleached with sodium chlorite was used to produce CMC and the mass gain was 35%. After 3 h reaction a white powder, denser than water, was obtained. A test of the water body was carried out (31) to verify CMC

Table 3
Bands of Characteristic Oscillations in IR Region for the Cellulose^a

Functional group	Type of deformation	Band region (cm ⁻¹)
-C-H; -CH ₂	Axial antisymmetrical, symmetrical	2926-2853
	Angular symmetrical in the plan and outside plan	1465-1350
	Angular antisymmetrical in the plan and outside plan	720-1150
-O-H	Axial	3550-3200
	Angular in the plan	1420-1330
	Angular outside plan	769-650
-C-O; C-O-C	Axial	1260-1000
Adsorbed H ₂ O	Angular symmetrical in the plan	Approx 1600

^aSee refs. 15 and 36.

affinity with the water. Water was put in a glass and CMC was added (spatula tip) to the water surface. After some minutes, CMC sample had a gelatinous aspect and soon afterward it was dissolved in the water.

CMC is a polar molecule with a great affinity for water. The dissolution of CMC in water confirmed the success in obtaining this material. The original cellulose (bleached pulp) does not dissolve in water. A CMC mass gain of 35% was observed, in other words, after the reaction the material was incorporated to the product. There is introduction of functional groups in the molecule chain of the cellulose. In the case of CMC, the hydrogen of the cellulose hydroxyl is substituted for the CH₂COONa group. The introduction of the functional group in the cellulose results in the obtainment of a product of molar mass higher than that of the original cellulose, causing a mass gain, corresponding to 23.6% of substitution or 0.70 CH₂COONa group per unit of glucose residue. The maximum theoretical value of substitution is 3, but this value reached up to 1.2 according to the literature (27,31).

Infrared Spectroscopy

IR spectroscopy has been largely used for the characterization of lignocellulosic materials and studied in some works involving characterization of the compounds with or without modification (32-34). Samples were analyzed by spectroscopy in IR region and cellulose characteristic bands are presented in Table 3.

Using the IR spectra of the Fig. 2, the evaluation of the substitution degree (DS) was made through the analysis of the absorption band in the 1600 cm⁻¹ area in relation to the band in the region of 901 cm⁻¹ (Absorbance [Abs] 1600/Abs901). A 901 cm⁻¹ band corresponds to the vibration of the O-C-O group involving the carbon-1 (anomeric) of the polysaccharides and does not suffer influence of the other groups (35). Abs1600/Abs901 ratios of 4.89 and 2.63 were obtained for commercial

CMCNa and CMC, respectively. Other methods of determination of the DS were not tested. It was calculated using the ratio values between the absorbances (1600/cm and 901/cm), and a 0.63 DS was obtained (value found using 1.18 DS of commercial CMCNa, according to Machado [31]).

Machado (31) determined the DS of CMCNa by conductometric titration, obtaining 1.18 DS for commercial CMCNa and 1.0 DS for CMCNa obtained by the author (isopropanol as solvent). In work accomplished by Silva (27), DS of CMCNa, produced using isopropanol and ethanol as solvents, was determined by potentiometric titration. DS of CMCNa (isopropanol) was 0.73, whereas DS using ethanol as solvent was 0.64. This fact shows that the result obtained in the present work (0.63 DS), using the IR technique, was similar to that determined by other methods and it was also similar to the result of DS calculated by the mass gain (0.70).

Conclusions

The mass gain of CMC was 35%, corresponding to 23.6% of substitution or 0.70 CH₂COONa group per unit of glucose residue (DS = 0.70). The IR spectra showed characteristic bands of CMC in the region of 1150–1000 cm⁻¹ typical of ethers and band in the region of 1650–1550 cm⁻¹ that differentiates basically the spectrum of the cellulose form of CMC. Using the IR technique it was possible to obtain a DS of 0.63, similar to that determined by other methods (conductometric titration, DS [1.00] and potentiometric titration, DS [0.63] and it was also similar to the result of DS calculated by the gain mass [0.70]).

Acknowledgments

The authors acknowledge financial support from Fundação de Amparo à Pesquisa do Estado Científico e Tecnológico (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

References

1. Ruzene, D. S. (2005), *PhD. Thesis*, Faenquil/Debiq, Lorena, Brazil.
2. Kleinert, T. N. (1974), *Tappi J.* 57, 99–102.
3. Aziz, S. and Sarkanen, K. (1989), *Tappi J.* 72, 169–175.
4. Young, R. A. and Akhtar, M. (1998), In: *Environmentally Friendly Technologies for the Pulp and Paper Industry*. Wiley, New York, pp. 5–69.
5. Gonçalves, A. R. and Ruzene, D. S. (2001), *Appl. Biochem. Biotechnol.* 91–93, 63–70.
6. Gonçalves, A. R. and Ruzene, D. S. (2003), *Appl. Biochem. Biotechnol.* 105–108, 195–204.
7. Shatalov, A. A. and Pereira, H. (2005), *Carbohydr. Polym.* 59, 435–442.
8. Paszner, L. and Cho, H. J. (1989), *Tappi J.* 72, 135–142.
9. Bendzala, J. and Kokta, B. V. (1995), *Wood Sci. Technol.* 29, 467–479.
10. Goyal, G. C., Lora, J. H., and Pye, E. K. (1992), *Tappi J.* 75, 110–116.
11. Raymond, A. Y. and Akhtar, M. (1998), In: *Environmentally Friendly Technologies for the Pulp and Paper Industry*. Wiley, New York.
12. Sarkanen, K. V. (1990), *Tappi J.* 73, 215–219.
13. McDonough, T. J. (1993), *Tappi J.* 76, 186–193.

14. Gilarranz, M. A., Oliet, M., Rodrigues, F., and Tijero, J. (1998), *Can. J. Chem. Eng.* 76(2), 253–260.
15. Fengel, D. and Wegener, G. (1989), In: *Wood Chemistry, Ultrastructure, Reactions*. Walter de Gruyter, Berlin.
16. Hon, D. N. S. (1996), Chemical modification of lignocellulosic materials. Marcel Dekker.
17. Heinze, T. (1998), *Macromol. Chem. Phys.* 199, 2341–2364.
18. Sjöström, E. (1993), In: *Wood Chemistry: Fundamentals and Applications*, Academic Press, New York.
19. Juste, K. E. and Majewicz, T. G. (1985), In: *Encyclopedia of Polymer Science and Engineering*. vol. 3, Wiley, New York, pp. 226–269.
20. Biswal, D. R. and Singh, R. P. (2004), *Carbohydr. Polym.* 57, 379–387.
21. Browing, B. L. (1963), In: *The Chemistry of Wood*. New York, Interscience.
22. TAPPI—Technical Association of the Pulp and Paper Industry (1985), TAPPI Standard Methods. T 236 cm-85 (kappa number).
23. TAPPI—Technical Association of the Pulp and Paper Industry (1982), TAPPI Standard Methods. T 230 om-82 (viscosity).
24. Rocha, G. J. M. (2000), *PhD. Thesis*, São Carlos/Universidade de São Paulo, Brazil.
25. TAPPI—Technical Association of the Pulp and Paper Industry (1999), TAPPI Standard Methods T 230 om-99 (brightness of pulps).
26. TAPPI—Technical Association of the Pulp and Paper Industry (1999), TAPPI Standard Methods. T 236 om-99 (samples prepared).
27. Silva, P. J. (1997), *MS Thesis*, São Carlos/Instituto de Química, Brazil.
28. Faria, L. F. F. (1994), *MS Thesis*, Faenquil/Demar, Brazil.
29. Biermann, C. J. (1996), In: *Handbook of Pulping and Papermaking*. Academic Press, San Diego.
30. Mosai, S., Wolfaardt, J. F., Prior, B. A., and Christov, L. P. (1999), *Bioresour. Technol.* 68, 89–93.
31. Machado, G. O. (2000), *MS Thesis*, São Carlos/Instituto de Química, Brazil.
32. Collier, W. E., Schultz, T. P., and Kalasinsky, V. F. (1992), *Holzforschung* 46(6), 523–528.
33. Kimura, F., Kimura, T., and Gray, D. G. (1992), *Holzforschung* 46(6), 529–532.
34. Ferraz, A., Rodriguez, J., Freer, J., and Baeza, J. (2000), *Bioresour. Technol.* 74, 201–212.
35. Morohoshi, N. (1991), In: *Wood and Cellulosic Chemistry* (Hon, D. N. S. and Shiraiishi, N., eds.). Marcel Dekker, New York, pp. 331–392.
36. Silverstein R. M. and Bassler. (1974) In: *G. C. Spectrometric Identification of Organic Compounds, 5th Ed.* John Wiley, New York.