Carboxymethyl Cellulose from Waste Lignocellulosic Pulps Produced by a Fast Soda/Aq Process

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ABSTRACT

Cellulose pulps were prepared from ground branch wood from pine and poplar and ground wheat straw by a fast soda/anthraquinone pulping. This process used high pulping temperatures and short residence times. Various combinations of temperature and time were used so that the H factor for pulps from pine and poplar was a constant 2700 while for pulps from wheat straw it was 270. The chemical composition of the resulting cellulose pulps was characterized and the possibility of synthesizing carboxymethyl cellulose from them was evaluated. The degree of substitution of our CMCs was found to be dependent upon the source of the lignocellullosic material, but independent of the pulping conditions for a specific substrate, (0.75 for pine, 0.82 for poplar and 0.89 for wheat straw). The rheological properties, the intrinsic viscosity and the molecular weight of the CMCs were found to be dependent on the pulping conditions for each lignocellulosic tested. The molecular weights of our CMC samples were 219,000 to 316,000 for pine, 335,000 to 375,000 for poplar, and 350,000 to 383,000 for wheat straw. The molecular weights were highest for the pulps cooked at low temperatures.

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INTRODUCTION

Carboxymethyl cellulose (CMC) is a cellulose-derived ether that is widely used as an additive in industrial applications because of its rheological properties in water solution. It is synthesized by the reaction of alkali cellulose with monochloroacetic acid or sodium chloroacetate[1,2] and 350,000 tm are produced annually throughout the world. Several grades of CMC are commercialized for multiple applications and the essential difference between them is the purity, degree of substitution and molecular weight. CMC is an additive in the manufacture of cements, glues and adhesives,[3] paints,[4] ceramics, textiles,[5-7] paper[8] and detergents. Technical-grade CMCs with degrees of substitution from 0.7 to 0.8 and with up to 20% of sodium chlorine are used in these applications. The formulation of drilling mud [9,10] is another extended application of CMC which uses technical grade CMCs that have degrees of substitution between 0.5 and 1.2 and that may have up to 40% of sodium chlorine. CMC is finding more and more applications in the pharmaceutical, medical and food industries. CMC is a key component in controlled drug-release pills and in the manufacture of personal care products.[11-13] It is used in gels that are applied as protecting agents during heart, thorax and cornea surgery.[14-16] CMC is also an approved food additive in the US and Europe. In the food industry it serves as a thickening agent in dairy products and sauces, as a stabilizer in frozen foods and ice creams,[17] and also as an important additive in low-calorie foods since it is not metabolized.[18] Essentially, high purity CMCs (>99%) with degrees of substitution from 0.7 to 1.0 are used in food and pharmaceutical applications.

Cellulose feedstocks for the production of CMC and other dissolving pulps are currently obtained from bleached, prehydrolyzed kraft and acid sulfite pulps. The cellulose pulps used in the manufacture of dissolving pulps require the following specifications: an α-cellulose contents above 90%, very low kappa numbers, low hemicellulose and ash contents, and viscosity-average degrees of polymerization in the range of 800 to 2500.[19] The average degree of polymerization required for CMC synthesis is between 800 to 1000.

Waste lignocellulosics such as low-quality wood and agriculture residues are a potential source of cellulose pulps that may meet the quality specifications required to synthesize some dissolving pulps. Residual lignocellulosics may be

used to manufacture dissolving pulps in geographical areas where good quality wood is scarce and large amounts of residual lignocellulosics like straws and other agriculture wastes are available at a very low cost. We demonstrated the feasibility of producing high-quality cellulose pulps from wheat straw by a fast alkali-pulping process.[20] This pulping process consisted of a two-stage treatment: impregnation of the lignocellulosic with the pulping chemicals at low temperature and high pressure, followed by pulping at high temperature and low contact time by direct steaming of the impregnated solid. In this work we have investigated the fast-pulping approach for the production of cellulose pulps suitable for CMC synthesis using three lignocellulosic residues: wheat straw and two low-quality (non-mature) woods.

MATERIALS AND METHODS

Lignocellulosic Materials

We used three different types of lignocellulosics to prepare the cellulose pulps:

a) Softwood: a batch of 50 kg of pine (*Pinus insignis*) was used. Small branches of pine were ground and sieved to 2 mm. The moisture content of the sieved material was around 8% (dry basis).

b) Hardwood: poplar (*Populus sp.*) was used. Small branches of poplar were ground and sieved to 2 mm before use. The moisture content of the sieved material was around 9% (dry basis)

c) Non-wood fibers: wheat straw (*Triticum aestivum*) was used as a typical source. Straw was also ground and sieved. The fraction collected between 2.0 and 0.32 mm was used in this study. The fines fraction (less than 0.32 mm) was discarded since it was rich in ash components.[20] The moisture content of the sieved material was 7% (dry basis).

The chemical composition of the lignocellulosics was measured using the methods described in the analytical methods section, and is presented in Table 1.

TABLE 1

Chemical Composition of the Residual Lignocellulosics.
Average Values and Confidence Intervals for a Probability Level of 95%
(Weight based on 100g of dry material)

	Pine	Poplar	Wheat straw
Ash	0.3 ± 0.0	4.3 ± 0.2	4.5 ± 0.1
Hot water extractives[1]	2.0 ± 0.2	10.1 ± 2.0	11.9 ± 0.4
Ethanol/toluene extractives	3.5 ± 0.6	2.7 ± 0.5	4.6 ± 0.5
Klason lignin[1]	26.2 ± 0.1	24.1 ± 0.6	14.2 ± 0.6
Glucose	42.6 ± 1.4	41.7 ± 1.8	33.0 ± 1.2
Xylose	5.7 ± 0.3	17.0 ± 1.9	18.8 ± 2.5
Galactose	4.0 ± 0.4	n.d. [2]	4.3 ± 1.6
Arabinose	3.3 ± 0.4	n.d. [2]	4.2 ± 1.2
Manose	11.3 ± 0.3	1.2 ± 0.1	4.6 ± 2.1
Holocellulose[1]	-	56.5 ± 0.2	-
α-Cellulose[1]	-		-

[1] Values corrected for ash content. [2] n.d.: not detected

Preparation of the Cellulose Pulps

Cellulose pulps were prepared by fast soda/AQ pulping in a stirred batch reactor with a capacity of 10L, which was constructed of ANSI 304-L and 316-L stainless steel. The reactor was equipped with a variable speed Magnedrive II stirrer (Autoclave Engineers, Erie, PA. USA), an internal coil for heating and cooling, and an inlet at the bottom so that steam could be added to the reacting mixture. The typical pulping cycle consisted of the following steps:

a) The lignocellulosic was impregnated with the pulping liquor at low temperatures under stirring at 750 rpm. This stirring was maintained throughout the pulping cycle.

b) The mixture was rapidly heated to the desired pulping temperature by adding saturated steam (40 bar and 240°C). With this procedure, the pulping temperature was usually reached in less than two minutes.

c) Isothermal pulping was carried out until the desired H factor was reached. Steam was not added to the mixture during this step, but the temperature of the reactor was maintained by controlling the flow rate of saturated steam through the inner coil.

d) Then fast cooling stopped the reaction. Once the target pulping time was reached the flow of steam through the inner coil was stopped, and tap water was circulated through the coil at a high flow rate.

Once cooled, the system was depressurized through a valve at the top of the reactor, and emptied into a 50L polypropylene container. It was thoroughly washed with deionized water until neutrality and these washings were quantitatively recovered. The yield of pulp for each experiment was calculated from the wet weight of the whole pulp and the moisture content of the pulp determined in three pulp samples. Moisture content was established by drying the pulp samples at 105°C until constant weight. The residual alkali contents of the liquor and pulp washings were estimated by titrating duplicate samples with a standard acid solution to a pH of 10.5,[21] from which the alkali consumed during the process was calculated.

Complete information on the impregnation and pulping conditions for the three lignocellulosics is presented in Table 2. The temperature-time profile was recorded for each experiment and used to calculate the H-factor at which the pulp was prepared. The values of the H factor were calculated using a modified equation suitable for alkaline pulping at zero sulfidity,[22] which is the case of soda/AQ pulping.

The cellulose pulps were bleached before the CMC derivatives were prepared. Bleaching was carried out by several consecutive treatments with sodium chlorite in acidic media. The procedure was similar to the one used for the preparation of chlorite holocellulose,[23] but it was performed at milder conditions to avoid an excessive degradation of cellulose.

Synthesis of Carboxymethyl Cellulose

The method that we used to prepare the carboxymethyl cellulose was adapted from the procedure described by Browning[24] for cotton linters. Cellulose was suspended in isopropyl alcohol under mechanical stirring at room temperature and 40% NaOH was added to the mixture. It was stirred for 90 min to yield alkali cellulose. Monochloroacetic acid was then slowly added for 30 min and the mixture was maintained at 55°C for 3.5 h. After this time, methanol (70% v/v) was added to the reactor, and the mixture was neutralized with acetic acid (90%).

TABLE 2

Impregnation and Pulping Conditions.

	Pine	Poplar	Wheat straw
Impregnation			
Load of lignocellulosic [1] (g)	500	500	500
Liquor to wood mass ratio	7.5:1	7.5:1	7.5:1
Alkali load (% on dry wood)	40	30	20
AQ load (% on dry wood)	0.1	0.1	0.1
Temperature (°C)	100	100	100
Time (min)	10	10	10
Pulping			
Liquor to wood ratio	9:1	9:1	9:1
Target H-factor	2700	2700	270
Temperature / time (°C / min)	170 / 92	170 / 92	150 / 60.0
	180 / 38	180 / 38	160 / 22.5
	190 / 15	190 / 15	170 / 8.0
	200 / 6	200 / 6	180 / 2.5
	205 / 3	205 / 3	

[1] Expressed as mass of dry solid.

The CMC fibers were then separated by filtration and washed six times with ethanol (70% v/v). Finally, the product was washed with pure methanol and oven dried at 60°C.

Analytical methods

The lignocellulosic materials and the cellulose pulps were analyzed using the following standard methods: ASTM D-1348 for moisture content; TAPPI T 15 os-80 for ash content; ASTM D-1111-84 for hot water extractives; ASTM D-1107-84 for organic extractives (i.e., soluble in an ethanol/benzene mixture), but benzene was replaced by toluene. Lignin content was measured as Klason lignin for the lignocellulosic substrates (ASTM D-1106-84), and by the kappa number method for cellulose pulps (TAPPI T-236 cm-85). Holocellulose content was determined by sodium chlorite delignification,[23] and α-cellulose was measured in

the hollocelulose samples according to the TAPPI T-203 om-93 method. The carbohydrate analysis was performed by acid hydrolysis of the samples,[25] and HPLC analysis of the hydrolysis products. The cellulose content was estimated from the amount of glucose in the hydrolyzate; a correction was introduced for glucomannans in the case of the softwood mixture, assuming that the mannose to glucose ratio was 3:1.[26] The intrinsic viscosity of the cellulose pulps was measured according to the ISO 5351/1-1981 standard method.

The samples of CMC were analyzed for purity and degree of substitution (DS). The purity of the different CMC samples was determined with to the ASTM D 1439-72 standard method. The degree of substitution was determined with a conductimetry method.[24] Intrinsic viscosity of the CMCs was measured in 0.1M NaCl at 25°C in a Cannon Fenske viscometer (series 100). Oven-dry (105°C) samples of CMC were dissolved in 0.1M NaCl and filtered through a 40 μm porous plate before being loaded into the viscometer. Intrinsic viscosity was calculated using a minimum of four CMC concentrations, and all measurements were made by triplicate. The rheological behavior of CMC in solution was studied using a HAAKE VT550 viscometer. Samples of dry CMC were dissolved in water at concentrations of 2% and then placed in the viscometer, which operated at 25°C. Deformation velocities varied between 11.7 and 1170 s^{-1} for each sample.

RESULTS AND DISCUSSION

Cellulose Pulps

Tables 3, 4 and 5 show the yield and chemical composition of the cellulose pulps from pine, poplar and wheat straw, respectively. Kappa numbers may be considered constant for each lignocellulosic substrate regardless of the pulping temperature. This is in agreement with the use of constant H-factor values and alkali loads during pulping. H-factors and other pulping conditions are summarized in Table 2.

The yield of pulp from pine wood was independent of pulping temperature in the interval used in this study (see Table 3). The average yield of pulp was 47% and the pulps had Kappa numbers around 25. The ash content of the pulps was

TABLE 3

Yield and Chemical Composition of the Pulps Produced from Pine Wood.
(Pulping Conditions in Table 2)

Pulp #	PI-01	PI-02	PI-03	PI-04	PI-05
Pulping					
Temperature (°C)	170	180	190	200	205
Time (min)	92	38	15	6	3
Residual Alkali (% initial)	56.4	53.2	48.2	53.0	55.6
Pulp yield (% of dry wood)	46.8	48.4	46.6	47.0	46.7
Pulp Composition					
(% based on dry pulp)					
Ash content	0.4	0.4	0.4	0.5	0.5
Kappa number	25.3	24.0	25.1	26.0	24.3
Residual Lignin	3.8	3.6	3.8	3.9	3.6
Glucose	81.3	81.6	83.5	83.4	83.8
Xylose	5.4	3.8	3.6	3.0	3.1
Mannose	9.2	10.4	8.9	9.0	9.2
Intrinsic viscosity (mL/g)	654	605	556	508	461
Bleached pulp					
Intrinsic viscosity (mL/g)	446	390	357	328	243

also independent of pulping temperature, but slightly higher than the ash content of the untreated pine wood (0.4 vs. 0.3 for pine wood). An increase in the pulping temperature affected the ratio between glucose and hemicellulosic sugars (xylose and mannose) to some extent. The mass-ratio glucose/xylose increased from 15 when the pulp was prepared at 170°C to 27 for the pulp obtained at 205°C. Meanwhile the mass-ratio of glucose/mannose remained at around 9.1, independent of pulping temperature. The main effect of raising the pulping temperature at constant H-factor was the decrease in the intrinsic viscosity of the pulp, which is a direct indication of a more acute depolymerization of cellulose during pulping. At a pulping temperature of 170°C, the intrinsic viscosity was 665 mL/g. When the pulping temperature decreased, the intrinsic viscosity decreased almost linearly to a value of 464 mL/g at 205°C.

Pulps prepared from poplar had kappa numbers around 20, and table 4 shows their complete characterization. The pulp yield decreased slightly with

TABLE 4

Yield and Chemical Composition of the Pulps Produced from Poplar Wood.
(Pulping Conditions in Table 2)

Pulp #	PO-01	PO-02	PO-03	PO-04	PO-05
Pulping					
Temperature (°C)	170	180	190	200	205
Time (min)	92	38	15	6	3
Residual Alkali (% initial)	32.5	33.3	33.0	32.2	38.4
Pulp yield (% of dry wood)	42.2	40.2	39.4	38.4	33.1
Pulp Composition					
(% based on dry pulp)					
Ash content	6.7	6.4	6.0	5.2	4.9
Kappa number	18.7	20.0	20.0	20.0	18.9
Residual Lignin	2.8	3.0	3.0	3.0	2.8
Glucose	71.3	71.6	74.1	76.2	78.7
Xylose	19.6	19.3	16.9	15.2	13.7
Holocellulose[1]	90.1	90.5	90.5	90.1	91.2
α-Cellulose[1]	73.0	72.0	74.6	75.1	77.8
Intrinsic viscosity (mL/g)	678	655	592	554	528
Bleached pulp					
Intrinsic viscosity (mL/g)	585	567	524	465	427

[1] Corrected for ash content

pulping temperature from 42% at 170°C to 38.4% at 200°C. Beyond this temperature the degradation of cellulose was much more intense, and the pulp yield decreased to only 33%. The maximum temperature that can be used practically to produce cellulose pulps from poplar at a high yield appears to be around 200°C. The ash content was high for these pulps due to the high ash content of the poplar sawdust selected as feedstock for the study. The ash content of the pulp decreased steadily with pulping temperature, from 6.7% for pulp PO-01 (170°C) to 4.9% for PO-05 (205°C). The increase in the pulping temperature resulted in higher cellulose and a lower hemicellulose content in the pulp. Thus, the weight ratio between glucose and xylose rose from 3.64 for pulp PO-01 to 5.74 for pulp PO-05. For the original hardwood, the glucose/xylose ratio was 2.5. The intrinsic viscosity of the pulps was also reduced when the pulp was prepared at higher temperatures, from 685 mL/g at 170°C to 529 mL/g at 205°C.

Table 5 shows the yield and characteristics of the pulps prepared from wheat straw. Kappa numbers were around 12 for all pulps, and pulp yield varied considerably with temperature. Yield dropped from 47% for the pulp prepared at 150°C to 43% for the pulp prepared at 160°C. Higher pulping temperatures had little effect on yield, and at 180°C pulp yield was 41%. The ash content of the pulp was around 2.7%, independently of the pulping temperature. The glucose content of the pulps shows that they were richer in cellulose when the pulping temperature was higher, while the content of hemicellulose-related sugars, mainly xylose, decreased. Consequently, the ratio of glucose to hemicellulose-sugars increased from 2.5 for pulp WS-01 to 2.8 for pulp WS-04. This ratio was 1.0 for wheat straw. The intrinsic viscosity of the pulps decreased slightly from 731 mL/g for pulp WS-01 (150°C) to 719 mL/g for pulp WS-04, which suggested that there was very little cellulose degradation during pulping. This result is consistent with the use of pulping temperatures below 180°C, since at higher temperatures cellulose in basic media depolymerizes to a considerable extent through hydrolytic cleavage.[22]

In general, bleached pulps had lower viscosity than unbleached pulps, especially for pine pulps the bleaching conditions were too severe resulting in some cellulose degradation. The intrinsic viscosity for bleached pine pulps ranged from 446 for pulp PI-01 (170°C) to 243 for pulp PI-05 (205°C). Poplar and wheat straw pulps were bleached in less severe conditions, and the bleached pulps had higher viscosity. For poplar, viscosity ranged from 585 for pulp PO-01 (170°C) to 427 for pulp PO-05 (205°C). The viscosity for wheat straw bleached pulps ranged from 665 for pulp WS-01 (150°C) to 556 for pulp WS-04 (180°C).

Carboxymethyl cellulose

Carboxymethyl celluloses prepared from the bleached pulps of pine, poplar and wheat straw were analyzed for purity, degree of substitution, intrinsic viscosity and rheological characteristics. Table 6 shows the CMC yield as a function of the temperature at which cellulose pulp was prepared. The CMC yield for pulps prepared from pine was 49%, regardless of the pulping temperature. Yields for poplar where slightly lower, around 47%, but they were also independent of the pulping temperature. The same was observed for wheat straw,

TABLE 5

Yield and Chemical Composition of the Pulps Produced from Wheat Straw.
(Pulping Conditions in Table 2)

Pulp #	WS-01	WS-02	WS-03	WS-04
Pulping				
Temperature (°C)	150	160	170	180
Time (min)	60	22.5	8	2.5
Residual Alkali (% initial)	23.1	27.1	28.2	30.1
Pulp yield (% of dry wood)	47.0	43.0	42.0	40.7
Pulp Composition				
(% based on dry pulp)				
Ash content	2.9	2.6	2.6	2.7
Kappa number	12.6	10.6	11.3	13.3
Residual Lignin	1.9	1.6	1.7	2.0
Glucose	67.4	67.4	69.9	70.1
Xylose	22.9	23.5	23.3	20.7
Mannose	3.9	4.2	4.3	4.0
Intrinsic viscosity (mL/g)	731	723	726	719
Bleached pulp				
Intrinsic viscosity (mL/g)	665	638	609	556

TABLE 6

Yield, Moisture Content, Purity and Degree of Substitution (DS) of
Carboxymethyl Cellulose from Pine, Poplar and Wheat Straw Bleached Pulps.

CMC sample [1]	Yield [2] (%)	Moisture (%)	Purity (%)	DS
Pine				
PI-01 (170°C)	49.1 ± 0.4	7.9	99.6	0.74 ± 0.02
PI-02 (180°C)	48.9 ± 0.2	7.9	99.5	0.76 ± 0.01
PI-03 (190°C)	48.5 ± 0.6	7.8	99.4	0.75 ± 0.01
PI-04 (200°C)	48.6 ± 0.3	7.9	99.5	0.75 ± 0.02
PI-05 (205°C)	49.0 ± 0.2	7.8	99.4	0.75 ± 0.02
Poplar				
PO-01 (170°C)	47.1 ± 0.2	7.8	99.5	0.82 ± 0.02
PO-02 (180°C)	46.9 ± 0.4	7.8	99.6	0.82 ± 0.01
PO-03 (190°C)	46.8 ± 0.5	7.8	99.4	0.83 ± 0.01
PO-04 (200°C)	46.9 ± 0.3	7.9	99.5	0.81 ± 0.03
PO-05 (205°C)	47.0 ± 0.1	7.8	99.6	0.81 ± 0.02
Wheat straw				
WS-01 (150°C)	55.2 ± 0.1	7.9	99.5	0.89 ± 0.01
WS-02 (160°C)	55.1 ± 0.2	7.8	99.3	0.88 ± 0.02
WS-03 (170°C)	54.9 ± 0.5	7.9	99.4	0.89 ± 0.01
WS-04 (180°C)	55.0 ± 0.3	7.9	99.5	0.90 ± 0.01

(1) Numbers in brackets are pulping temperatures. (2) Based on dry bleached pulp

with an average yield of 55%. The purity of the CMC preparations was higher than 99.3% in all cases, well above the purity of 98% required for commercial pure-grade CMCs. The moisture content of our CMC preparations, dried at room temperature, was around 8%, which is a typical value for commercial-grade CMC. The degrees of substitution were also independent of the pulping temperature in the range of conditions tested in our study, but they were significantly different among the CMCs prepared from cellulose pulps of the different species. The degree of substitution was lowest for CMCs from pine pulps (0.75), and highest for CMCs from wheat straw pulps (0.89). CMCs prepared from poplar pulps have an intermediate degree of substitution of 0.82. Those results show that our CMC preparations are well within the typical limits of purity, moisture and degree of substitution for commercial-grade CMCs.

Besides the degree of substitution, the viscosity and rheological behavior of a specific CMC in aqueous solution also determine its potential uses. Figure 1 plots the reduced viscosity of the five CMCs prepared from pine pulps against the concentration in 0.1M NaCl at 25°C. The intrinsic viscosity of these CMCs is obtained from the extrapolated intercepts at zero concentration. Table 7 presents the intrinsic viscosity in 0.1M NaCl at 25°C of all the CMCs prepared from pine, poplar and wheat straw pulps. All substrates have similar trends: the intrinsic viscosity drops when the pulping temperature is high. Because the cellulose pulp was prepared at higher temperatures the extent of cellulose depolymerization during the soda/AQ pulping was more severe, and the pulps produced had lower intrinsic viscosities. Consequently, the CMCs synthesized from these pulps also had a lower molecular weight, and hence a lower intrinsic viscosity.

The viscosity-average molecular weight for our CMCs was calculated using the Mark-Houwink-Sakurada relationship (equation 1). The intrinsic viscosity of three commercial CMC samples of known molecular weight was determined (Figure 2) and equation 1 was used to relate the intrinsic viscosity of the commercial CMCs in 0.1M NaCl at 25°C with their molecular weight. The correlation was reasonable (see figure 3), with k=8.32 10^{-4} g/mL, a=1.06 and a correlation coefficient of 0.978. This expression is valid for CMCs with a degree of substitution between 0.7 and 0.9. Parameter a is close to 1, which is typical value for cellulose and its derivatives.[27] The values for parameter k are dependent on the degree of substitution and the molar mass of CMC, the concentration of
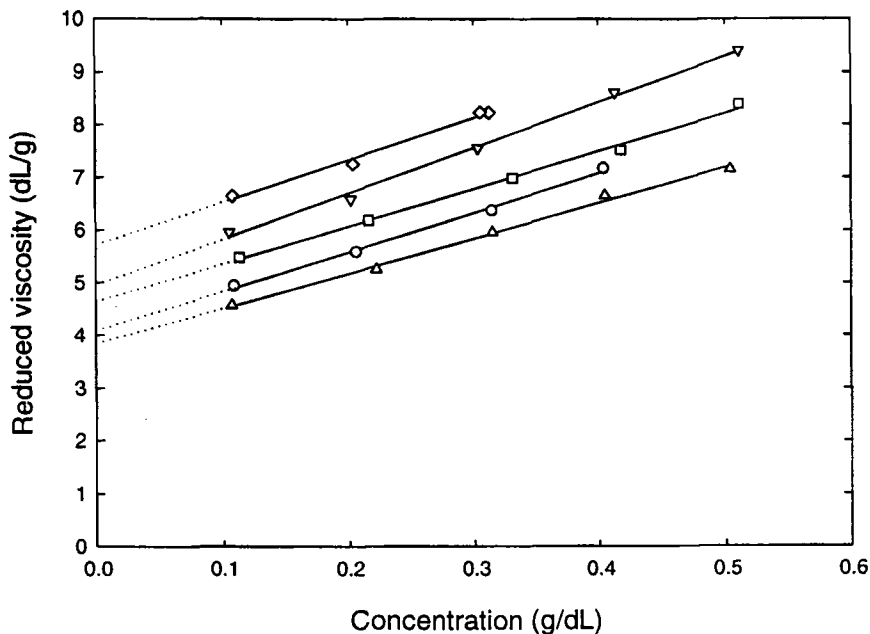
Figure 1. Reduced viscosity versus concentration for pine-derived CMCs in NaCl 0.1M at 25°C. (Symbols identify temperature of pulping: ◇ 170°C, ▽ 180°C, ☐ 190°C, ○ 200°C and △ 205°C)

NaCl and the temperature of the solution. Typical values of parameter k for CMCs range from $1.0 \ 10^{-4}$ to $4.3 \ 10^{-2}$ g/mL.[27]

The average molecular weight values for the CMCs prepared from pine, poplar and wheat straw pulps are shown in Table 7. Molecular weights ranged from 219,000 to 316,000 for pine-derived CMCs; from 350,000 to 375,000 for poplar CMCs and from 350,000 to 383,000 for those CMCs prepared from wheat straw pulps. All of these values are scattered around 250,000, which is considered to be an intermediate molecular weight for commercial-grade CMC.

$$[\eta] = k \ M_w^{\ a} \tag{1}$$

TABLE 7

Intrinsic Viscosity [η], Average Molecular Weight (M_w) and Coefficients for the Ostwald-de-Waele Equation for CMCs from Pine, Poplar and Wheat Straw.

CMC[1]	Intrinsic viscosity [η] (mL/g)	Average molecular Weight M_w	Ostwald-de-Waele equation (2% CMC in water)		
			m (Pa s ^{n})	n	R^2
Pine					
1 (170°C)	585	316,000	1.47 (0.10)	0.646 (0.011)	0.9989
2 (180°C)	500	272,000	1.43 (0.11)	0.652 (0.012)	0.9985
3 (190°C)	474	250,000	1.09 (0.07)	0.677 (1.010)	0.9991
4 (200°C)	406	224,000	0.61 (0.03)	0.745 (0.008)	0.9996
5 (205°C)	396	219,000	0.70 (0.05)	0.718 (0.010)	0.9993
Poplar					
1 (170°C)	703	375,000	8.95 (0.40)	0.513 (0.008)	0.9989
2 (180°C)	692	370,000	8.05 (0.30)	0.526 (0.007)	0.9992
3 (190°C)	685	366,000	8.18 (0.39)	0.514 (0.009)	0.9988
4 (200°C)	671	350,000	7.53 (0.20)	0.506 (0.005)	0.9996
5 (205°C)	623	335,000	6.59 (0.28)	0.526 (0.008)	0.9991
Wheat straw					
1 (150°C)	719	383,000	4.80 (0.51)	0.587 (0.019)	0.9958
2 (160°C)	705	376,000	4.78 (0.35)	0.579 (0.013)	0.9979
3 (170°C)	696	372,000	5.13 (0.50)	0.558 (0.018)	0.9961
4 (180°C)	651	350,000	3.63 (0.56)	0.610 (0.028)	0.9923

[1] Numbers in brackets are pulping temperatures.

The rheological properties of our CMCs were studied in a rotary viscometer at 25°C. CMC samples were dissolved in water at a concentration of 2%. Figures 4, 5 and 6 plot the shear stress (Pa) against shear rate (s⁻¹) for the CMC samples prepared from pine, poplar and wheat straw pulps, respectively. The data from the rheograms were adjusted to the Ostwald-de-Waele equation for pseudoplastic fluids (equation 2), where τ_{yx} (Pa) is shear stress, dv_x/dy is the shear rate, m is the consistency index and n is the flow behavior index. Table 7 shows the values of m, n and the correlation coefficient, R^2, for each CMC sample. There was agreement between the experimental data and equation 2, indicating that CMC in water solution behaves like a pseudoplastic fluid. The values of the flow behavior index, n, for CMCs prepared from pine pulps ($0.70 \leq n \leq 0.78$) indicate
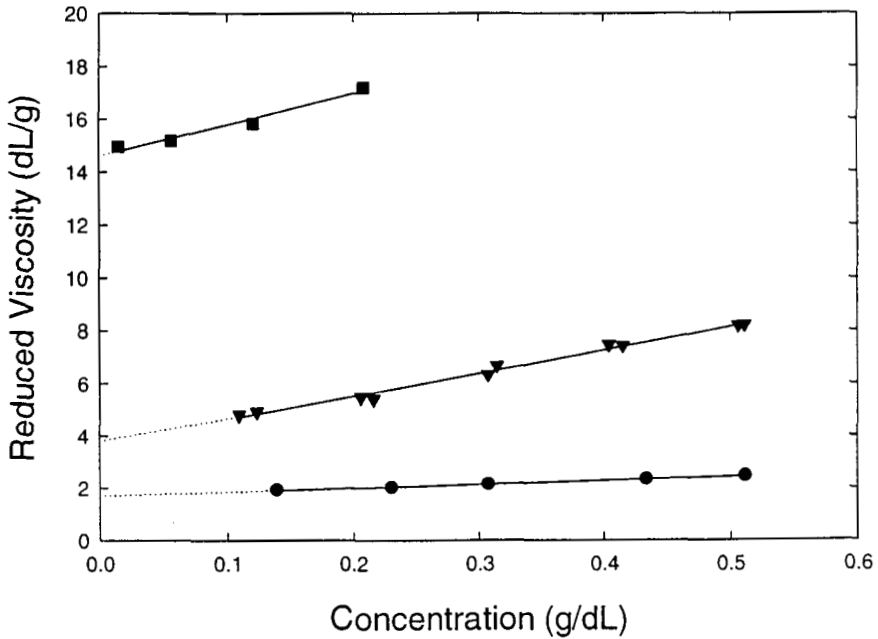
Figure 2. Reduced viscosity versus concentration of commercial CMC of different molecular weights in NaCl 0.1M at 25°C. ■ M_w 700,000; ▼ M_w 250,000; and ● M_w 90,000.

that this particular lignocellulosic gives CMCs with flow properties closer to a Newtonian fluid than those from poplar ($n \cong 0.53$) and wheat straw ($n \cong 0.55$). The degree of polymerization of the preparations influences the rheological characteristics of the CMC to a certain extent. For CMCs prepared from the same lignocellulosic species, and at a specific shear rate, the shear stress increases with molecular weight.

$$\tau_{yx} = -m \left| \frac{dv_x}{dy} \right|^{n-1} \frac{dv_x}{dy} \tag{2}$$
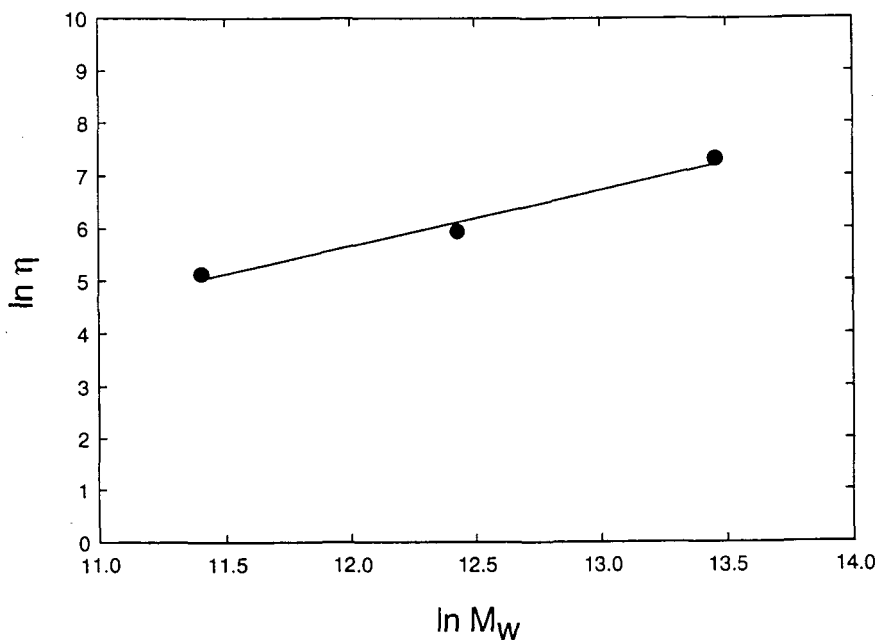
Figure 3. Mark-Houwink-Sakurada plots of commercial CMC in NaCl 0.1M at 25°C.
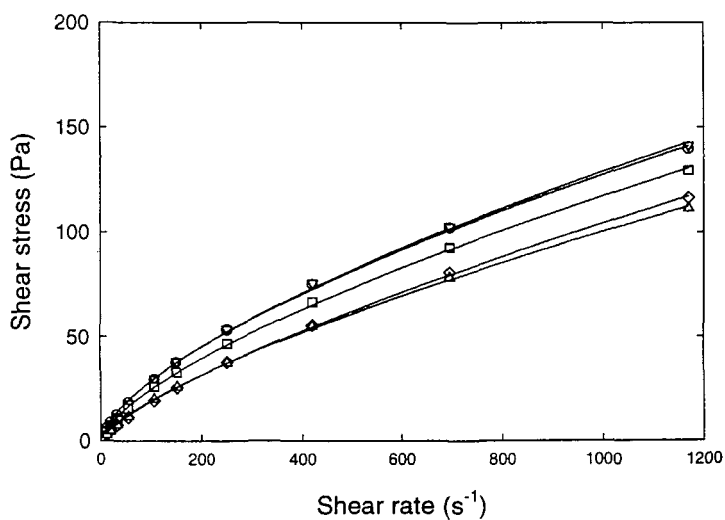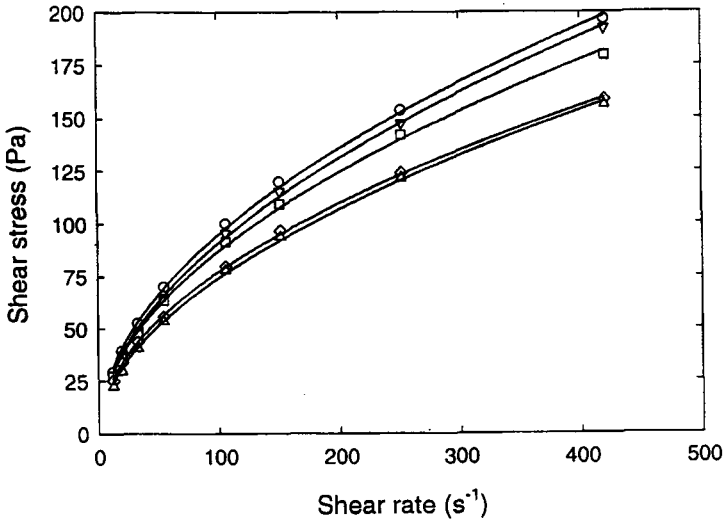

Figure 4. Shear stress-shear rate relationship for CMC from pine pulps in 2% aqueous solution at 25°C (Open symbols identify the preparation temperature of pine pulps: ◇ 170°C, ▽ 180°C, □ 190°C, ○ 200°C and △ 205°C)

Figure 5. Shear stress-shear rate relationship for CMC from poplar pulps in 2% aqueous solution at 25°C (Open symbols identify the preparation temperature of poplar pulps: ◇ 170°C, ▽ 180°C, □ 190°C, ○ 200°C and △ 205°C)
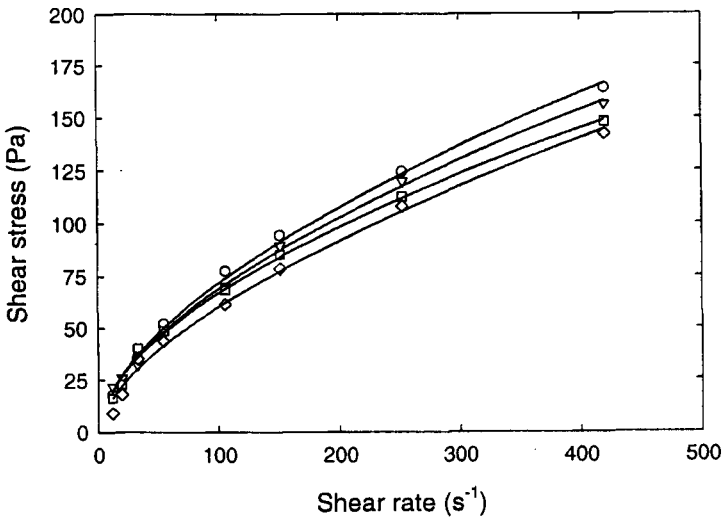

Figure 6. Shear stress-shear rate relationship for CMC from wheat straw pulps in 2% aqueous solution at 25°C (Open symbols identify the preparation temperature of wheat straw pulps: ◇ 170°C, ▽ 180°C,□ 190°C and ○ 200°C)

CONCLUSIONS

The results of fast pulping of pine, poplar and wheat straw using short pulping times at high temperatures show that pulps with a high degree of delignification, and typical yields can be obtained. The use of a constant H-factor ensures the same level of residual lignin in the pulps. Pulping temperature plays an important role since pulp viscosity decreases almost linearly with temperature. Thus, pulping temperature can be used to control the molecular weight of cellulose, which is the main factor in determining the rheological properties of the CMCs. The degree of substitution of CMCs depends on the pulp raw material but does not on the pulping conditions. The whole set of results indicates that fast soda anthraquinone pulps can be used for the preparation of commercial-grade carboxymethyl cellulose. Based on their degree of substitution and rheological characteristics, CMCs from pine pulps (DS of 0.75) could be used in paper and textile applications. CMCs from poplar (DS of 0.82) could find applications in the manufacture of detergents, fertilizers and paints. Finally, CMCs from wheat straw (DS of 0.89) show potential as additives for food products, personal care products, and for biomedical applications. Our CMC preparations will be intensively tested in the future to ensure that they are suitable for specific applications.

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