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Preparation and characterisation of methylcelluloses from *Miscanthus sinensis*

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Abstract

Methylcelluloses were prepared and characterised from *Miscanthus sinensis* (elephant grass). *M. sinensis* pulps were prepared by impregnation rapid steam pulping process (IRSP) and bleached by a total chloride free (TCF) sequence using hydrogen peroxide. Aldrich α-cellulose was used as a model material to find a suitable methylation method for bleached pulps. The methylcelluloses were synthesised via double methylation with iodomethane in isopropanol slurry at 60 °C for 22 h. The supramolecular substitution patterns were determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy and the intrinsic viscosities were measured in 4% NaOH solution. The rheological properties were measured in either dimethyl sulphoxide (DMSO) or 4% NaOH solution and were similar to commercial methylcelluloses in distilled water. Water-soluble and alkali-soluble methylcellulose yields were determined by solvent extraction. This investigation helped to find the proper conditions for methylating bleached pulps prepared from *M. sinensis* and showed that high-quality methylcelluloses can be prepared from *M. sinensis*.

Keywords: Cellulose; Impregnation; IRSP pulping; Methylation; Methylcellulose; Miscanthus sinensis; Steam explosion; TCF bleaching

1. Introduction

The total global production of paper and paperboard increased from 268,515,320 metric tons in 1994 to 323,474,519 metric tons in 2002 (FAOSTAT Statistics database, 2003; www.fao.org). In 2002, about 52% was prepared from wood, principally the virgin wood (www.fao.org, 2003). Because of the overproduction of agricultural crops and the shortage of wood, non-woody materials such as annual plants and agricultural residues have received more attention in recent years for producing pulp, paper, paperboard, and cellulose derivatives (Barba, 2002; Ye and Farriol, 2005a; Ye et al., 2005). In fact, non-woody materials have been used to produce pulp and paper ever since the invention of papermaking (Atchison and McGovern, 1987). Wood is more expensive and more difficult to transport than non-woody materials, although non-woody materials have problems of collection, storage, and high ash contents (McDougall et al., 1993; Ilvessalo-Pfäffli, 1995). For economic and environmental considerations, as well as the fact that it provides higher yields of cellulose (Han and Rowell, 1996), non-wood is now gradually substituting wood as an alternative source of paper, paperboard, and cellulose derivatives (Barba, 2002; Ye and Farriol, 2005a, in press; Ye et al., 2005).

Miscanthus sinensis was introduced into Europe from China and Japan as an ornamental plant during the 1930s (Barba, de la Rosa, Vidal, Colom, Farriol and Montané, 2002). *M. sinensis* is usually planted and cultivated to produce energy because of its fast growth, high yield, and few soil and cultivation demands in Europe (Nick and Emmanuel, 2000). *M. sinensis* has been reported to yield between 20 and 26 dry tons per hectare, depending on the condition of the soil (Nick and Emmanuel, 2000). This elephant grass contains 87% of small parenchyma cells, which leads to a high content of primary fines in the pulp and secondary fines during the beating (Fukuda and Hishikawa, 1996; Ilvessalo-Pfäffli, 1995). Investigations have shown that *M. sinensis* is a promising source of pulp in the Mediterranean area (Barba et al., 2002; Iglesias et al., 1996; Vega et al., 1997). It has been shown to be an effective

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bioenergy crop and a high-quality source of paper (Barba et al., 2002; Fukuda and Hishikawa, 1996; Iglesias et al., 1996; Vega et al., 1997). Nowadays, *M. sinensis*' innovative investigations concentrate on achieving higher yield, better selectivity, and improved quality with sulphur-free pulping technologies, chlorine-free bleaching sequences, and new applications (Barba, 2002; Caridad et al., 2004; Fukuda et al., 2001; Ligeroa et al., 2005; Velasquez et al., 2003; Ye and Farriol, 2005a).

Methylcelluloses are usually prepared from either cotton or wood pulps in industrial companies (Brandt, 1986). Cotton is used to produce high viscosity methylcelluloses while wood pulps are used for lower viscosity methylcelluloses (Brandt, 1986). In the present investigation, a new material resource, the annual plant *M. sinensis*, which is principally used for the bioenergy application (Nick and Emmanuel, 2000), will be explored and evaluated its feasibility for producing methylcelluloses.

In this investigation, the first step was pulping, which separated stalk components in order to obtain cellulose. Pulps for the cellulose derivatisation must have high cellulose contents, low lignin contents, proper molecular weights, and capacities to dissolve in common cellulose solvents (Brandt, 1986). Steam explosion pulping with rapid impregnation has proved to be an effective method for producing pulps for the papermaking or dissolving pulps for the cellulose derivatisation (Barba, 2002; Montane et al., 1996). Therefore, this impregnation rapid steam pulping process is used in the present investigation.

Methylcellulose is important cellulose ether, which is mainly used in the construction and food industries as a functional additive (Brandt, 1986; Donges, 1990; Kennedy, 1985). Suida first synthesised methylcellulose in 1905 (Croon and Manley, 1963). Since then, many researchers (Hirrien et al., 1996; Kern, Choi, Wenz, Heinrich, Ehrhardt and Mischnick, 2000; Kondo and Gray, 1991; Philipp et al., 1979; Takahashi et al., 1987; Tapia, Sapag, Andrade, Hasson, Valenzuela and Basulato, 2002) have successfully prepared it in either heterogeneous or homogeneous media. In industry, methylcellulose is produced by methylation with methyl chloride in heterogeneous reaction media at high pressure (Brandt, 1986; Donges, 1997). On a laboratory scale, dimethyl sulphate and iodomethane are used because of their straightforward operation and apparatus (Brandt, 1986; Croon and Manley, 1963; Tapia et al., 2002). The reactivity and toxicity of dimethyl sulphate are higher than those of iodomethane (Brandt, 1986; Croon and Manley, 1963; Tapia et al., 2002). When our aim was to evaluate the feasibility and key parameters of preparation of methylcellulose from *M. sinensis*, iodomethane, a less reactive agent, was very suitable for synthesizing a series of samples with satisfactorily amplified property differences, which made it easier to compare and choose the process parameters and product properties.

2. Experimental

2.1. Fibre material and chemicals

Experiments were carried out using a homogeneous batch of dry *M. sinensis* stalks harvested in Galicia, northern Spain. The moisture content was about 8%. The stalks were chipped and stored in a commercial cooler below 0 °C before they were impregnated and their chemical compositions were analysed. For the composition analysis, sawdust with a maximum size of 0.4-mm mesh was used after further milling. All chemicals were bought from Sigma-Aldrich Co. as reagent grade.

2.2. Equipment

The chipping was carried out in a GA100 miller supplied by Black and Decker Co. The impregnation was carried out in a 2 l batch vessel made of ANSI 304-L and 316 stainless steel, which had a jacket connected to a commercial recycling hot water bath. At the top of the impregnation reactor, there was a tube connected to a high-pressure nitrogen bottle.

Rapid steam pulping was carried out in a batch reactor made in our laboratory, which consisted of two vessels that were connected by a short tube with a valve. One vessel was used for direct cooking with saturated steam at a high temperature and pressure. This vessel was connected with two tubes to supply the saturated steam for the reactor and a jacket, respectively. Another vessel was used for receiving materials that underwent a sudden pressure decompression. A steam boiler with a maximum temperature of 250 °C supplied the saturated steam.

The methylation reaction was carried out in a reaction flask over an AGIMATIC-E hot plate supplied by J. P. Selecta S. A. The reaction flask was connected to a coiled reflux condenser using tap water as coolant.

The viscosities and rheological data were obtained at 20 °C with a DIN Viscometer Visotester@550 supplied by ThermoHaake Co. The intrinsic viscosities were measured in an Ubbelohde viscometer combined with a 170226 Visocclock supplied by SCHOTT_GERÄTE GmbH in a water bath at 25 °C for pulps or 20 °C for methylcelluloses.

^{13}C NMR spectra were measured in a Gemini 300 spectrometer by using a 10 mm probe and deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent at 80 °C. The spectral conditions were taken from the investigation of Takahashi et al. (1987). The spectra were obtained by using a spectral width of 24.0 kHz, a repetition time of 3 s, a flip angle of 45°, and accumulated scans of 20,000 (Takahashi et al., 1987).

2.3. Experimental process

The chipped *M. sinensis* stalks were impregnated in 30% sodium hydroxide solution under 15 bar nitrogen pressure at

60 °C for 2 h. The ratio of solid to liquid was set so that the chipped stalks were almost completely submerged under the liquid. After the impregnation, the stalks and liquors were collected and weighed. The impregnated stalks were stored in a refrigerator. A sample of liquor was collected in order to measure the residual sodium hydroxide in the impregnated stalks by titration (Barba et al., 2002; Montane et al., 1996).

The maximum time between the impregnation and the steam pulping was 1 day. The impregnated stalks were directly heated by the saturated steam in the steam explosion reactor at various retention times and temperatures. The temperature and time were combined into a single parameter, the pulping severity, *p*-factor, which was calculated by the following Eq. (1) (Chornet and Overend, 1988):

$$P = \log(R_0) = \log\left(\int_0^t \exp(\frac{T-100}{14.75})\mathrm{d}t\right) \quad (1)$$

R_0 is the severity of steam pulping; T the reaction temperature, °C; t the retention time, min.

The pulps were collected by filtration and washed several times with distilled water until the pH value was nearly 7. All the unbleached pulps were dried in an oven at 60 °C to constant weights.

The pulps were bleached using an EPP sequence (E stands for alkaline extraction and P stands for hydrogen peroxide bleaching). During the alkaline extraction, pulps were extracted with 10% sodium hydroxide solution for 1 h at ambient temperature (about 20 °C) with a consistency of 3–4%. After this extraction, the pulps were collected by vacuum filtration and washed with distilled water. The hydrogen peroxide bleaching was performed with a consistency of 3–4% in 0.2 M NaOH and 0.15 M H_2O_2 solution for 1 h at 60 °C. At the end of the bleaching, the pulps were washed with distilled water until their pH values were nearly 7 and collected by filtration. The bleached pulps were dried in an oven at 60 °C to constant weights.

Aldrich α-cellulose was used in the preliminary experiments to find a suitable method for methylating the bleached pulps of *M. sinensis*. α-Cellulose was mercerised in 5, 10, 15, 20, 30, and 40% sodium hydroxide solution, respectively, for 1 h at ambient temperature (about 20 °C). After the mercerisation, the cellulose was collected by vacuum filtration and washed several times to a pH near 7 with distilled water. Then, the cellulose was dried in an oven at 60 °C to a constant weight. The iodine adsorption method was used to determine the accessibility of the celluloses (Browning, 1967; Hon and Yan, 2001).

The bleached pulp or commercial α-cellulose, about 5 g of dry weight, was mercerised in 100 g of 40% sodium hydroxide solution for 1 h at room temperature (about 20 °C) to form alkali cellulose. The alkali cellulose was filtered and pressed until the weight ratio of pulp and sodium hydroxide solution was 1:5. After the filtration, the alkali cellulose, 150 ml 2-propanol, and a certain volume of iodomethane were added to the reaction flask. The alkali cellulose was methylated in 2-propanol slurry at 60 °C for 22 h. Since the degree of substitution of methylcellulose was not high enough after one mercerisation and methylation, a second mercerisation and methylation was performed. After the reactions, the methylcellulose was collected by filtration, neutralised with acetic acid, and washed three times with acetone and ethanol, respectively. Finally, the synthesised methylcellulose was dried overnight in an oven at 60 °C and stored in a refrigerator at 4 °C for further analysis.

2.4. Characterisation

2.4.1. Composition of the Miscanthus sinensis stalk

The *M. sinensis* stalk was analysed by following standard procedures: ASTM D 1102—84 for ash content, ASTM D 1111—84 for hot-water extractives, modified ASTM D 1107—84 for ethanol/toluene organic extractives, ASTM D 1106 for Klason lignin, ASTM D 1104—56 for holocellulose, and ASTM D 1103—60 for α-cellulose.

2.4.2. Analysis of pulps

The kappa number of the pulps was determined by TAPPI T 236 om-99. The viscosity of the pulps was determined by TAPPI T 230 om-99 (capillary viscometer method). The intrinsic viscosity of the pulps was estimated by the Schula–Blaschke equation (Browning, 1967; Hon and Yan, 2001). The accessibility of the cellulose for the methylation reaction was determined by the iodine absorption method (Browning, 1967; Hon and Yan, 2001).

2.4.3. Analysis of methylcellulose

The methylcellulose was dried in an oven at 105 °C until a constant weight and dissolved in deuterated DMSO (DMSO-d6) at 80 °C. For each methylcellulose sample, the degree of substitution (DS) of methylcellulose was determined by ^{13}C nuclear magnetic resonance in deuterated dimethyl sulphoxide solution at 80 °C for 6 h. The methylcellulose peak signals (Fig. 1) were assigned in accordance with the work of Hirrien et al. (1996); Takahashi et al. (1987).

The viscosity of methylcellulose was determined by the capillary viscometer or rational viscometer in either dimethyl sulphoxide (DMSO) or 4% NaOH solutions. The intrinsic viscosity of methylcellulose was measured in 4% NaOH solution and calculated by plotting a serial of concentrations versus reduced viscosities. The water-soluble and alkali-soluble methylcellulose yields were determined by solvent extraction with distilled water and 4% NaOH solution, respectively. In order to estimate the intrinsic viscosity of methylcellulose, the relation of the viscosity and the intrinsic viscosity of methylcellulose was fitted at a concentration of either 0.5 or 2% in 4% NaOH solution.

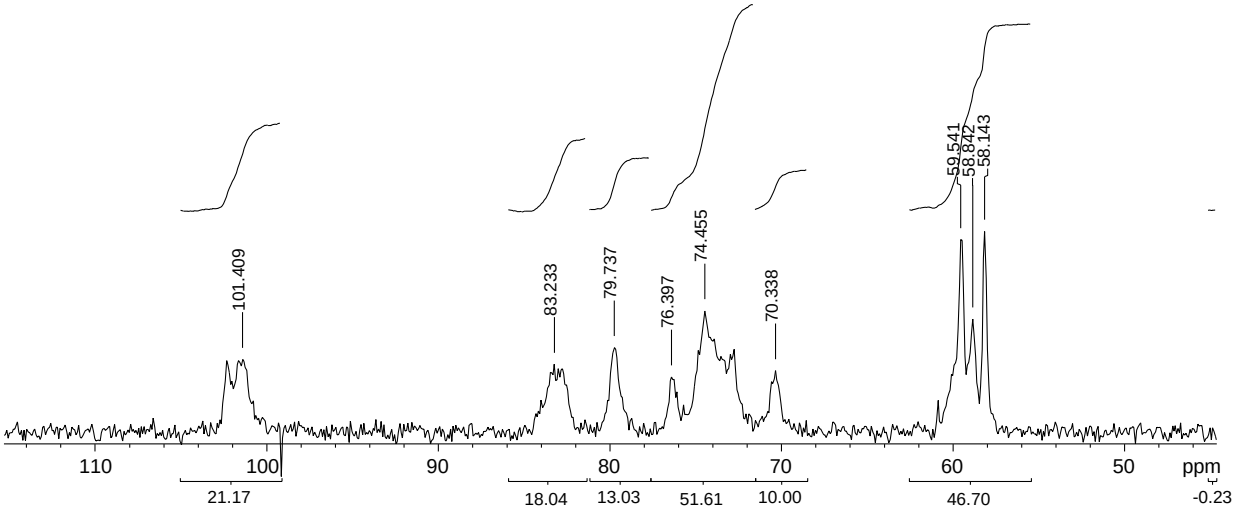

Fig. 1. ^{13}C NMR spectrum of MD-26 prepared from *Miscanthus sinensis*.

3. Results and discussion

3.1. Compositions and impregnation

The composition results based on the oven-dried weight (ODW) of the original material are listed in Table 1 (Barba, 2002). *M. sinensis* had high holocellulose and α-cellulose contents. It had a lower ash content than straw has, and a lower klason lignin content than wood has (Han and Rowell, 1996). These data show that *M. sinensis* has considerable potential in the production of dissolving pulps as well as in energy applications (Nick and Emmanuel, 2000).

The designed experimental parameters and the residual alkali in the impregnated fibre are shown in Table 2. The object of this impregnation was to uniformly distribute sodium hydroxide and anthraquinone (AQ) in the interior of porous chipped stalks, and therefore to obtain swollen *M. sinensis* chipped stalks. Table 2 shows that 44.6% of NaOH was absorbed in the *M. sinensis* stalks. This residual NaOH may be considered as the main pulping chemical in the subsequent cooking with saturated steam. The high pressure of 15 bars and intermediate temperature (about 60 °C) facilitated the penetration and diffusion of NaOH solution and AQ in the chipped stalks during the impregnation. Therefore, the impregnation time was reduced to 2 h while the usual impregnation needed 24 h under ambient pressure at about 20 °C (Barba, 2002). After the impregnation, the swollen and softened stalks were obtained. The colour of the impregnation liquid was observed to change from colourless at the beginning to black at the end, which is because the lignin was degraded and then it dissolved in the impregnation solution.

Table 1
Composition of the *Miscanthus sinensis* stalk

Component	Percent[a]
Ash	0.7
Water extractives	3.1
Organic extractives	9.1
Klason lignin	19.9
Holocellulose	72.5
α-Cellulose	42.2

[a] Oven-dried weight.

3.2. Rapid steam pulping

Pulping parameters and results are shown in Table 3. The kappa numbers, yields, and lignin contents of the pulps decreased as the *p*-factors increased, which show that the *p*-factor is the most important parameter of the steam pulping process. Their kappa numbers ranged from 6.5 to 14.1, and all were very low, which meant that the lignin contents were also low (Browning, 1967). After the impregnation and the rapid steam pulping, most of the lignin was eliminated. Their pulp yields were nearly 60% and relatively higher than the yields of usual chemical pulping methods (Fengel and Wegener, 1984). What is more important was that these pulps had almost no rejects, which had the advantage of eliminating the cost due to the screening equipment and its operations (Fengel and Wegener, 1984). Their intrinsic viscosities ranged from 1183 to 737 ml/g, which were suitable for further applications as paper, board, and dissolving pulps after bleaching (Brandt, 1986). These data show that this IRSP

Table 2
Experimental parameters and result of impregnation

Solid/liquid ratio	9
AQ (%)[a]	0.1
NaOH solution concentration (%)	30
Retention time (h)	2
Temperature (°C)	60
Residual alkali[b] (%)	44.6

[a] Oven-dried weight of *Miscanthus sinensis* stalk.
[b] Based on the initial NaOH charge.

Table 3
Steam pulping results

No.	*p*-factor	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g)
1	2.96	14.1	58.3	2.12	1183
2	3.26	9.3	57.2	1.40	957
3	3.53	8.3	56.3	1.25	864
4	4.06	6.5	55.8	0.98	737

Table 4
Results of TCF bleached *Miscanthus sinensis* pulps

No.	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g)
1	7.0	85.7	1.05	727
2	4.6	84.2	0.69	601
3	4.5	81.3	0.68	514
4	3.1	78.6	0.47	414

process can successfully produce pulps with excellent properties from *M. sinensis*.

3.3. Bleaching

Bleaching results are listed in Table 4. The properties of the bleached pulps were strong influenced by the pulping conditions when the bleaching condition was the same as for the *M. sinensis* pulps. The kappa numbers, yields, lignin contents, and intrinsic viscosities of the bleached pulps decreased as the pulping severities increased. The kappa numbers of the bleached pulps ranged from 3.1 to 7.0, which are low values although peroxide is not a highly active bleaching chemical (Fengel and Wegener, 1984). The lignin contents of the bleached pulps were lower than 1.1%. The yields of the bleached pulps were about 80%. The intrinsic viscosities of the bleached pulps ranged from 414 to 727 ml/g, which were suitable and sufficient for the cellulose derivatisation after three stages of alkaline treatments (Brandt, 1986). All these bleaching results showed that this TCF bleaching sequence, EPP, is effective and feasible for the *M. sinensis* pulps produced by the IRSP process. These bleaching data also showed that these bleached *M. sinensis* pulps can be used to synthesise methylcellulose or other cellulose derivatives (Barba, 2002; Brandt, 1986).

3.4. Methylation

3.4.1. Preliminary experiments with α-cellulose

The accessibilities of the α-celluloses treated by the mercerisations are shown in Fig. 2. As the NaOH concentrations of the mercerisation solutions increased, the accessibilities increased considerably after the α-celluloses were treated by the mercerisations. The best mercerisation

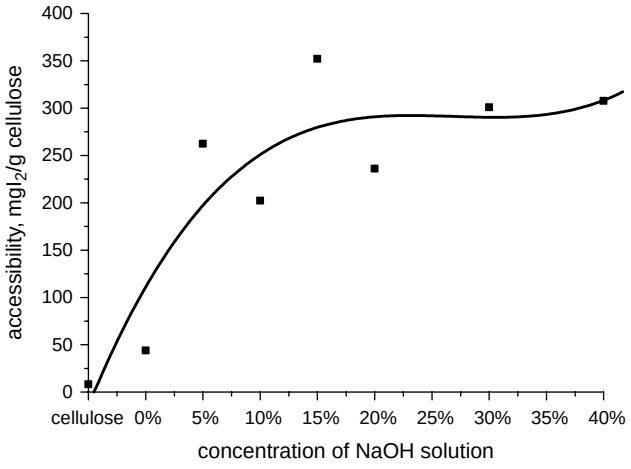

Fig. 2. Accessibilities of α-celluloses treated by mercerisations (*milligrams of adsorbed iodine per gram of cellulose).

result was obtained in 15% NaOH solution. However, after the α-celluloses was mercerised in 15% NaOH solution, there were still some unaccessible and crystalline regions in the α-cellulose. Hence, the excess sodium hydroxide solution should be retained after the mercerisation so that alkali cellulose can be completely formed during the subsequent methylation and the synthesis of methylcellulose has sufficient alkaline solution to proceed (Brandt, 1986).

α-Cellulose was mercerised in 15 and 40% sodium hydroxide solutions, respectively. Then, the mercerised cellulose was collected by vacuum filtration and then methylated with 50 ml iodomethane at 60 °C for 22 h in 2-propanol slurry. The obtained α-cellulose methylcelluloses were compared only for their solubilities in dimethyl sulphoxide. It is assumed that methylcellulose can be completely dissolved in DMSO when its degree of substitution is between 0.4 and 2.0 (Croon and Manley, 1963). The α-cellulose methylcellulose prepared from 40% sodium hydroxide solution completely dissolved in DMSO while the α-cellulose methylcellulose prepared from 15% sodium hydroxide solution only partly dissolved. This showed that 40% sodium hydroxide solution was better for mercerisation than 15% sodium hydroxide solution.

A total of 5-g dry weight of α-cellulose was mercerised and then methylated with 30 ml of iodomethane in the first methylation. Then in the second methylation, the volumes of iodomethane were varied in an attempt to find a better methylation condition. These results are listed in Table 5. As the added volumes of iodomethane increased, water-soluble methylcellulose contents increased. All α-cellulose methylcellulose samples were soluble in 4% NaOH solution at 20 °C, which meant that they were alkali-soluble methylcelluloses and all the crystalline cellulose participated in the methylation reaction. All α-cellulose methylcellulose samples were partially soluble in distilled water at 20 °C, which meant that some separation methods such as extraction, dialysis, or membrane separation were required to obtain water-soluble methylcelluloses.

Table 5
Solubilities and viscosities of α-cellulose methylcelluloses

Methylcellulose	MD17	MD15	MD18	MD21	MD23
Mole ratio of CH_3I/AHG	4.51	9.03	13.54	18.06	22.57
Water-soluble content (%)	32.40	39.88	34.19	71.96	75.61
4% NaOH solubility	Complete	Complete	Complete	Complete	Complete
DMSO solubility	Partly	Complete	Complete	Complete	Complete
Viscosity in 4% NaOH (mPas)	4.05	8.01	15.4	4.71	5.23
Intrinsic viscosity (ml/g)	166.4	483.3	800.0	205.6	227.6

AHG stands for anhydroglucose.

In order to empirically estimate the intrinsic viscosity from the viscosity measured in an alkaline solution, the viscosities and intrinsic viscosities of the α-cellulose methylcellulose were measured in 4% NaOH solution, respectively. The concentration of α-cellulose methylcellulose solution was 0.5%. The empirical equation was expressed as equation (2).

$$V = K \times \mathrm{IV}^{A} \tag{2}$$

where V is the viscosity of methylcellulose in 4% NaOH solution; K and A are constants; IV is the intrinsic viscosity measured in 4% solution.

Based on the above data, two constants were fitted and calculated as $K=0.065$ and $A=0.80$. So, the viscosity of 0.5% alkali-soluble methylcellulose in 4% NaOH solution can be estimated as equation (3)

$$V = 0.065 \times \mathrm{IV}^{0.80} \tag{3}$$

The degrees of substitution of the α-cellulose methylcelluloses are listed in Table 6. The average degrees of substitution of the α-cellulose methylcelluloses increased as the added iodomethane volumes increased. The data showed that the substitution at the 2-OH group was easier than the substitution at the 3-OH and 6-OH group. The substitution at the 3-OH group was easier than or the same as the substitution at the 6-OH group. As the molar ratios of iodomethane and anhydroglucose increased, the degrees of substitution at the 6-OH group increased more than the DS at the 3-OH group, which indicated that an increase of added volume of the methylation agent led to a better methylation reaction, a higher degree of substituent, and a better substitution distribution on the anhydroglucose unit of cellulose (Croon and Manley, 1963). The higher degree of substituent and the better substitution distribution of a methylcellulose lead to a better solubility in a variety of solvents (Croon and Manley, 1963).

Table 6
DS of α-cellulose methylcelluloses

Methyl-cellulose	Mole ratio of CH_3I/AHG	DS_2	DS_3	DS_6	DS
MD15	9.03	0.48	0.32	0.25	1.05
MD18	13.54	0.50	0.39	0.27	1.16
MD21	18.06	0.52	0.36	0.29	1.17
MD23	22.57	0.56	0.36	0.36	1.28

Methylcelluloses prepared from α-cellulose were dissolved in dimethyl sulphoxide as 1% solutions. Their shear-stress values were plotted versus their shear rates, as shown in Fig. 3. The solution properties of 1% α-cellulose methylcellulose in DMSO were quite different because of different molecular weights and degrees of substitution. All the solutions of the α-cellulose methylcelluloses with lower intrinsic viscosities (MD17, MD21, and MD23) seemed to be Newtonian types. The rheological data of α-cellulose methylcelluloses with higher molecular weights (MD18 and MD15) seemed to be pseudoplastic. The dilute solution properties of the α-cellulose methylcelluloses in 4% NaOH solution are shown in Fig. 4. The viscosities of all the α-cellulose methylcelluloses in the diluted solutions increased as the solution concentrations increased. The α-cellulose methylcelluloses with higher molecular weights had higher viscosities even at very low concentrations.

Considering all the above preliminary α-cellulose methylations, the best condition for synthesising methylcellulose was a mercerisation in 40% NaOH solution at ambient temperature (about 20 °C) for 1 h and then a methylation with 50 ml iodomethane per 5 g cellulose in 150 ml 2-propanol slurry at 60 °C for 22 h.

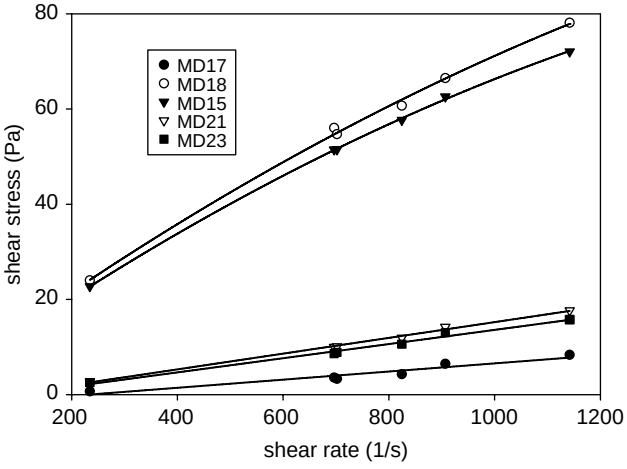

Fig. 3. Rheological properties of 1% α-cellulose methylcelluloses in DMSO.

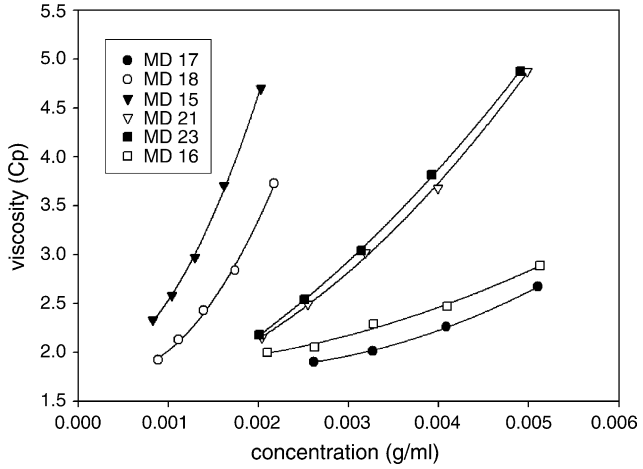

Fig. 4. Dilute solution properties of α-cellulose methylcelluloses in 4% NaOH solution.

3.4.2. Methylation of bleached M. sinensis pulps

The methylation conditions and analysis results are listed in Table 7. The water-soluble methylcellulose contents increased as the steam pulping retention times increased. Four methylcellulose samples (MD25, MD22, MD24, and MD19) were completely soluble in 4% NaOH solution, which meant they were complete alkali-soluble methylcelluloses and all the cellulose in the pulp participated in the methylation. All the methylcellulose samples were partially soluble in water, which meant that further separation was needed to purify the methylcelluloses. The viscosities of the methylcelluloses in 4% NaOH solution increased as the steam pulping retention times increased. Table 7 shows that all the yields of alkali-soluble methylcelluloses were very high. The yields of water-soluble methylcelluloses, however, were lower. Table 7 shows that the methylcellulose yields, contents, and solubilities can be improved if the steam pulping time or the pulping severity is increased.

In order to empirically estimate the intrinsic viscosity from the viscosity measured in an alkaline solution, the viscosity and the intrinsic viscosity of the *M. sinensis* methylcellulose were measured in 4% NaOH solution, respectively. The concentration of methylcellulose for measuring the viscosity was 2%. The empirical equation was expressed as equation (2). Based on these data, two constants were fitted and calculated as $K = 0.00082$ and $A = 2.01$. Hence, the viscosity of 2% alkali-soluble methylcellulose in 4% NaOH solution can be estimated as equation (4)

$$V = 0.00082 \times \mathrm{IV}^{2.01} \quad (4)$$

Table 8 shows the DS of methylcelluloses prepared from M. sinensis. It can be seen that the M. sinensis pulps were more difficult to synthesise than the commercial α-cellulose. This is due to the existence of trace lignin and the special aggregated fibril structure in the bleached pulp, in which the accessibility of cellulose is hindered by them (Krassig, 1993; Ye and Farriol, in press). Therefore, the *M. sinensis* pulps had less accessibilities and reactivities than the α-cellulose had. Table 8 shows that the methylation was easier for the *M. sinensis* pulps that contained less trace lignin and were pulped by a higher pulping severity, *p*-factor. This is due to that the higher pulping severity can lead to a pulp with less trace lignin and more accessible cellulose, which facilitates the diffusion and penetrate of both the NaOH solution and the methylation reagent in the porous fibrils of the obtained pulp (Ye and Farriol, in press).

The methylation was easier at the 2-OH group than other OH groups. As the steam pulping retention time increased, so did the degrees of substitution (DS) at all three OH groups. Hence, the average total DS increased. For the *M. sinensis* methylcellulose that had a lower total DS (less than 1.00), DS at the 6-OH group was higher than the DS at the 3-OH group. For the *M. sinensis* methylcellulose that had an intermediate total DS, DS at the 6-OH group was very nearly the same as the DS at the 3-OH group. For the *M. sinensis* methylcellulose with the highest total DS value, the DS at the 6-OH group was higher than the DS at the 3-OH group. The DS at the 3-OH group was lower than the DS at the 2-OH group because of the blocking effect of the vicinal 2-OH group.

The rheological figures of the *M. sinensis* methylcelluloses are plotted in Figs. 5 and 6 in 4% NaOH solution and water, respectively. A15 is a commercial methylcellulose obtained from the DOW Company. Another commercial sample (Aldrich 14,000) was bought from the Aldrich Company with an average molecular weight of 14,000.

Table 7
Methylation conditions and results of *Miscanthus sinensis* pulps

Methylcellulose	MD25	MD22	MD24	MD19	MD26
Pulp sample	1	2	3	4	4
1st Mole ratio of CH_3I/AHG	22.6	13.5	18.1	13.5	22.6
2nd Mole ratio of CH_3I/AHG	22.6	13.5	18.1	13.5	22.6
Alkali MC yield (%)	93.1	83.8	93.8	95.4	87.7
Water-soluble MC yield (%)	23.2	71.7	68.2	56.1	85.2
Alkali MC content (%)	100	100	100	100	90.5
Water-soluble MC content (%)	22.1	69.2	84.1	53.6	93.4
Viscosity in 4% NaOH (mPas)	4.48	20.6	4.48	165	94.4[a]
Intrinsic viscosity (ml/g)	65.5	155.3	84.1	435.5	210.3

[a] 2% solution in distilled water.

Table 8
DS of *Miscanthus sinensis* methylcelluloses

Methyl-cellulose	Steam pulping time (min)	DS_2	DS_3	DS_6	DS
MD25	4	0.20	0.09	0.17	0.46
MD22	8	0.33	0.16	0.21	0.70
MD24	15	0.40	0.34	0.32	1.06
MD19	26	0.43	0.36	0.35	1.14
MD26	26[a]	0.67	0.38	0.47	1.52

[a] Higher volume of iodomethane in methylation.

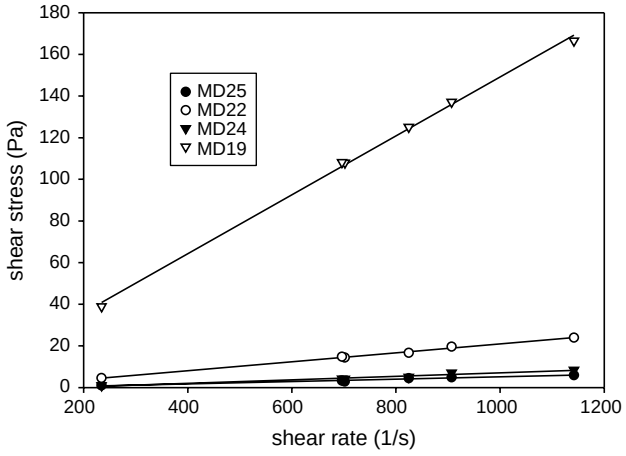

Fig. 5. Rheological properties of 2% *Miscanthus sinensis* methylcelluloses in 4% NaOH solution.

These two samples were not pre-treated, and were dissolved in hot distilled water and then cooled to 20 °C. The data in Figs. 5 and 6 show that their curve tendencies were similar though their viscosities and substituted patterns were different. All these rheological data seemed to increase linearly to be Newtonian types. This indicated that the 4% NaOH solution is a true solvent for a low molecular weight methylcellulose with a low degree of substitution (Croon and Manley, 1963). These data demonstrate that

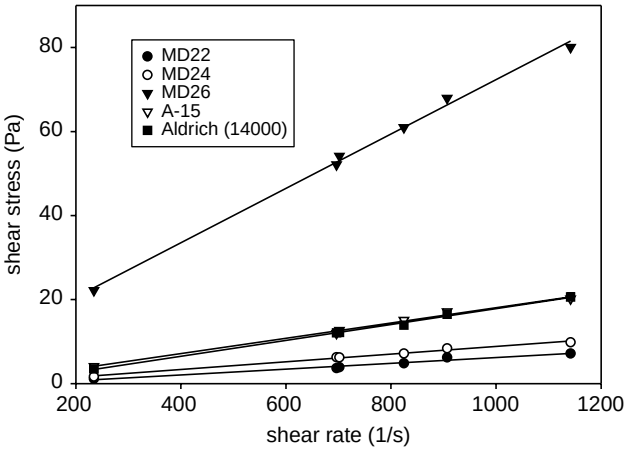

Fig. 6. Rheological properties of 2% *Miscanthus sinensis* methylcelluloses in distilled water.

the properties of methylcelluloses prepared from *M. sinensis* are similar to those of the commercial methylcelluloses.

4. Conclusion

A proper methylation method was found using the commercial α-cellulose. The prepared methylcelluloses were a mixture of alkali-soluble and water-soluble methylcellulose. As the added volume of iodomethane increased, so did the DS and water-soluble methylcellulose contents. When the pulping severities increased, the DS and the water-soluble methylcellulose contents also increased. Most methylcellulose solutions in 4% NaOH and DMSO seemed to be Newtonian. This investigation successfully prepared and characterised methylcelluloses from *Miscanthus sinensis*, which proved that the pulping severity was the key factor in the production of pulps, and perhaps even the main factor that influenced the properties of prepared methylcelluloses. This research demonstrated that the fast-growth *Miscanthus sinensis* should be an alternative raw material for producing methylcelluloses rather than low-growth wood.

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