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Preparation and characterisation of methylcellulose from annual cardoon and juvenile eucalyptus

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Abstract

We have studied the preparation of methylcellulose from annual cardoon and juvenile eucalyptus. The high cellulose and low lignin contents of these plants make them potential alternative resources for cellulose derivation. Their high quality pulps were obtained by the Impregnation Rapid Steam Pulping (IRSP) process and Total Chloride Free (TCF) bleaching sequences using hydrogen peroxide. The bleached pulp was methylated twice in an isopropanol slurry at 60 °C for 22 h after mercerisation in 40% NaOH solution. Yields of water-soluble and alkali-soluble methylcellulose were determined by solvent extraction. Substitution patterns of methylcellulose were determined by ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy. The intrinsic viscosities and solution properties of methylcellulose were measured in either 4% NaOH solution or dimethyl sulphoxide (DMSO). This study shows that annual cardoon and juvenile eucalyptus can produce high-quality methylcellulose, which can be used as alternative resources for the production of methylcellulose.

Keywords: Cardoon; Eucalyptus; IRSP pulping; Methylation; Methylcellulose; TCF bleaching

1. Introduction

Annual cardoon (*Cynara cardunculus*) is a herbaceous perennial plant belonging to the compositae family (Antunes, Amaral, & Belgacem, 2000; Gominho, Fernandez, & Pereira, 2001). It is originally from the Mediterranean region and usually grows in a warm, temperate climate. It can also survive arid situations (http://www.nf-2000.org). Cardoon is scattered over a wide region in Spain, France, Italy and other Mediterranean countries. It has been used in regional food dishes (e.g. in soups and salads), but mainly as an enzymatic source for milk coagulation in traditional cheese making (Antunes et al., 2000; Dalianis, Panoutsou, & Dercas, 1996; Gominho et al., 2001; Pereira, Miranda, Paes, & Gominho, 1994; Pereira, Gominho, & Miranda, 1994). Its average production is 20 tons/ha per year, with about 40% stalks, 25% leaves, and 35% capitulas (Fernandez, 1992; Fernandez & Curt, 1995). In recent years cardoon has been shown to be a potential pulping and energy resource in southern Europe (Antunes et al., 2000; Benjelloun, Lopez, & Delmas, 1998; Dalians, Christou, Sooter, Krytsis, Zafiris, & Samiotakis, 1994; Fernandez & Curt, 1995; Pereira, Miranda et al., 1994; Pereira, Gominho et al., 1994; Piscioneri, Sharma, Baviello, & Orlandini, 2000; Gominho et al., 2001).

Cardoon is perfectly adapted to Spain's continental conditions (Antunes et al., 2000; Benjelloun et al., 1998; Dalians et al., 1994; Fernandez & Curt, 1995; Gominho et al., 2001; Pereira, Miranda et al., 1994; Pereira, Gominho et al., 1994; Piscioneri et al., 2000). The Spanish government plans to promote renewable energy, so they are promoting a plantation of 1,000,000 ha of energy crops to substitute petroleum in the future (Fernandez, 1998). Cardoon has been selected as one of the potential crops. If this plan gets under way, cardoon will be planted and harvested to a considerable quality in Spain, so new applications of cardoon other than for energy would be marketable and feasible and have sufficient supply.

Eucalyptus is originally from Australia but adapts well to cultivation in many climates. Today over 13,000,000 ha of eucalyptus are planted in over 70 counties (Davidson, 1993;

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Montagu, Kearney, & Smith, 2003). The eucalyptus is usually cultivated to produce energy and pulps or for domestic applications, since it grows quickly and does not require best soil conditions or much cultivation (Nick & Emmanuel, 2000). Pulps or cellulose made from a young two-year-old eucalyptus improve land utilisation and produce higher cellulose yields than a usual eucalyptus of several years.

Methylcellulose is an important cellulose ether (Donges, 1990; Brandt, 2001). Methylcellulose has been used in the cement, pharmaceutical and food industries for many years, not only because it can be used as an emulsifier, medicine or medicine constituent, colloidal stabiliser, viscosity controller and flow controller, but also because it is non-toxic (Greenway, 1994; Greminger, 1979; Greminger & Krumel, 1981; Guo, Skinner, Harcum, & Barnum, 1998; Brandt, 2001). Worldwide production of methylcellulose is about 150,000 t/y (Donges, 1990; Heinze & Liebert, 2001). The application of methylcellulose depends not only on its molecular weight or viscosity in water, but also on its degree of substitution (DS) (Donges, 1990). Methylcellulose of low molecular weight can be used as a surfactant or coating (Kokubo, Obara, & Nishiyama, 1998), while methylcellulose of high molecular weight can be used as a viscosity controller (Donges, 1990; Greenway, 1994; Greminger, 1979; Guo et al., 1998). Methylcellulose with a DS between 0.1 and 1.0, which can dissolve in dilute aqueous 2–10% NaOH solution (Croon & Manley, 1963; Brandt, 2001), can be used for the treatment of textiles (Maasberg, 1946; Jahn, 1952). Methylcellulose with a DS between 1.3 and 2.6, which can dissolve in cold water (Brandt, 2001; Croon & Manley, 1963), has a greater production and many more applications (Donges, 1990; Greenway, 1994; Greminger, 1979; Guo et al., 1998; Brandt, 2001).

The methylation of cellulose is carried out according to the Williamson ether synthesis (Donges, 1990; Fengel & Wegener, 1984; Brandt, 2001). In industries, methylcellulose is produced in heterogeneous media with methyl chloride (Brandt, 2001). In laboratories, methylcellulose is usually synthesised from dimethyl sulphate and methyl iodine using suitable apparatus and processes (Croon & Manley, 1963). In this paper, we prepared methylcellulose by a suitable methylation method developed in our laboratory (Ye & Farriol, 2003; Ye & Farriol, 2005).

More valued cellulosic products, which are produced from young two-year-old eucalyptus and cardoon planted in marginal and set-aside lands, will of course up-grade the low-grade biomass and utilisation of lands (Fernandez, 1992; Fernandez & Curt, 1995; http://www.nf-2000.org). In this paper, we study two challenging new materials-annual cardoon (harvested both in spring and in summer) and juvenile eucalyptus. We evaluate the feasibility of using them to produce methylcellulose, which is for the first time to be investigated.

2. Experimental

2.1. Plant materials and chemicals

Experiments were carried out using a homogeneous batch of the two-year-old eucalyptus and the spring cardoon stalks with leaves and capitula, both of which were grown in Spain. IRSP pulps of dry summer cardoon stalks were used. The bark of the eucalyptus chips was removed by hand. The moisture contents of the eucalyptus chips and the cardoon chips, as measured, were 20.05 and 10.36%, respectively. To analyse composition, the sawdust with a maximum size of 0.4-mm-mesh was used in order to ensure a kinetic and non-diffusion control during the measurements. All chemicals were bought from Sigma-Aldrich Co. as reagents grade.

2.2. Equipment

Stalks were chipped in a GA100 miller supplied by Black and Decker Co. The impregnation was carried out in our laboratory in a 2-l batch reactor. The impregnated chips were steam-cooked in our laboratory in a stainless steel reactor. The methylation reaction was carried out in a reaction glass flask over a heat plate of Agimatic-E supplied by J. P. Selecta S. A.

Viscosities and rheological data were measured by a DIN Viscometer Visotester@550 supplied by ThermoHaake Co. at 20 °C. The intrinsic viscosities were measured in an Ubbelohde viscometer combined with a 170226 Viscoclock supplied by SCHOTT_GERÄTE GmbH in a water bath at 25 °C for pulps and 20 °C for methylcellulose. The ^{13}C-NMR spectra were obtained in a Gemini 300 spectrometer operating at 300 MHz.

2.3. Experimental processes

The spring cardoon chips were impregnated in 30 or 20% sodium hydroxide solutions under 15 bars nitrogen pressure at 55 °C. The eucalyptus chips were impregnated in 30% sodium hydroxide solution under 15 bars nitrogen pressure at 55 °C for 2 h. The weight ratio of chips and liquid was adjusted so that the chips would be completely immersed in the liquid. Anthraquinone (AQ) was added as 0.1% of the oven-dried weight of the chips. The impregnated chips and liquors were collected and weighed. The impregnated chips were stored in a cooler at 4 °C. The residual sodium hydroxide absorbed in the impregnated chips was determinated by the titration method.

The maximum interval between the impregnation of the chips and their subsequent cooking was one day. The temperature and time of cooking were combined into one parameter, the *p*-factor, which was calculated from the following Eq. (1) (Chornet & Overend, 1988):

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

where R_0 is the severity of pulping, the *p*-factor; *T* is the cooking temperature in degrees centigrade; and *t* is the retention time in minutes.

The impregnated chips were directly cooked by saturated steam according to a series of *p*-factors with varied cooking times and temperatures. The cooking chips were suddenly decompressed into a container. Suspected pulps were collected by filtration and washed several times by the distilled water until the pH value was nearly 7. All unbleached pulps were dried in an oven at 60 °C.

The bleaching sequences for the cardoon pulps were PP or PEP (E stands for alkaline extraction and P stands for hydrogen peroxide bleaching). The bleaching sequence for the eucalyptus pulps was PP. The unbleached pulps were extracted by 10% sodium hydroxide solution at the ambient temperature for one hour with 3–4% consistency. After this alkaline extraction, the pulps were collected by vacuum filtration and washed with the distilled water. The hydrogen peroxide bleaching was performed with 3–4% consistency in 0.2 M NaOH and 0.15 M H_2O_2 solution for 1 h at 60 °C. After bleaching, the pulp was washed in distilled water until the pH value was almost 7 and collected by filtration. The bleached pulps were dried in an oven at 60 °C.

Five grams of bleached pulp (based on dry weight) was mercerised in 100 g 40% sodium hydroxide solution for 1 h at room temperature (roughly 20 °C). The mercerised pulp was filtered and pressed until the weight ratio of the pulp and sodium hydroxide solution was 0.2. Upon the filtration, the mercerised pulp, 150 ml 2-propanol and 50 ml iodomethane were added to a flask. The methylation reaction lasted for 22 h at 60 °C. The mercerisation and methylation were repeated twice. After methylation, the methylcellulose was collected by vacuum filtration, neutralised with acetic acid and washed three times with acetone and ethanol, respectively. Finally, the methylcellulose samples were stored in a cooler at 4 °C.

2.4. Characterisation

2.4.1. Composition analysis of the cardoon and eucalyptus

The compositions of the cardoon and eucalyptus were determined by the following standard procedures: ASTM D 1102-84 for the ash content, ASTM D 1111-84 for the hot water extractives content, modified ASTM D 1107-84 for the ethanol/toluene organic extractives content, ASTM D 1106 for the Klason lignin content, ASTM D 1104-56 for the holocellulose content and ASTM D 1103-60 for the alpha-cellulose content.

2.4.2. Analysis of the pulps

The kappa number was determined according to TAPPI T 236 om-99. The residual lignin content was estimated to be the value than the kappa number times 0.15, and there is a linear relationship between kappa number and lignin content over a wide range (Brauns, 1952; Browning, 1967). The intrinsic viscosities of pulps were determined according to ISO 5351-1, 1981.

2.4.3. Analysis of methylcellulose

The methylcellulose sample was dried in an oven at 105 °C until the weight was constant and dissolved in the deuterated DMSO (DMSO-d6) at 80 °C. The DS of methylcellulose was determined by the ^{13}C nuclear magnetic resonance spectroscopy in the deuterated dimethyl sulphoxide solution at 80 °C for 6 h for each methylcellulose sample. The spectra were obtained using a spectral width of 24.0 kHz, a repetition time of 3 s, a flip angle of 450 and accumulated scans of 20,000 (Takahashi, Fujimoto, Miyamoto, & Inagaki, 1987). Peak signals of methylcellulose (Fig. 1) were assigned according to the work of Takahashi et al. (1987). The viscosity of methylcellulose was determined by either a capillary viscometer or a rational viscometer in either dimethyl sulphoxide or 4% NaOH solution at 20 °C. The intrinsic viscosity was measured in DMSO or 4% NaOH solution at 20 °C. The yields of water-soluble and alkali-soluble methylcellulose were determined at 20 °C in the distilled water and 4% NaOH solution, respectively.

3. Results and discussion

3.1. Compositions

The compositions of the spring cardoon and eucalyptus are listed in Table 1. The water extractive content of the spring cardoon was as high as 26.7%, which may be because the spring cardoon was harvested with capitula, leaves and stalks. Many water-soluble materials coexisted in the spring cardoon stalks. The ash content of the spring cardoon was higher than that of the eucalyptus. Spring cardoon had a lower lignin content than the eucalyptus, which means that the pulping severities of cardoon should be lower than the pulping severities of eucalyptus. The cellulose content of the spring cardoon was lower than that of the eucalyptus. These data indicate that the leaves and capitula of the spring cardoon must be eliminated before the pulping. The holocellulose content of the eucalyptus was as much as 71%, while the holocellulose content of the spring cardoon was 48.3%. These results show that the juvenile eucalyptus has a strong potential to produce paper or dissolving pulp as well as energy and that some pre-treatment of the spring cardoon is needed before it can be applied.

3.2. Impregnation

The experimental parameters and residual NaOH in the impregnated chips are shown in Table 2. The residual NaOH in the impregnated chip increased as the impregnation time and concentration of the sodium hydroxide solution increased. When the concentration of the NaOH solution

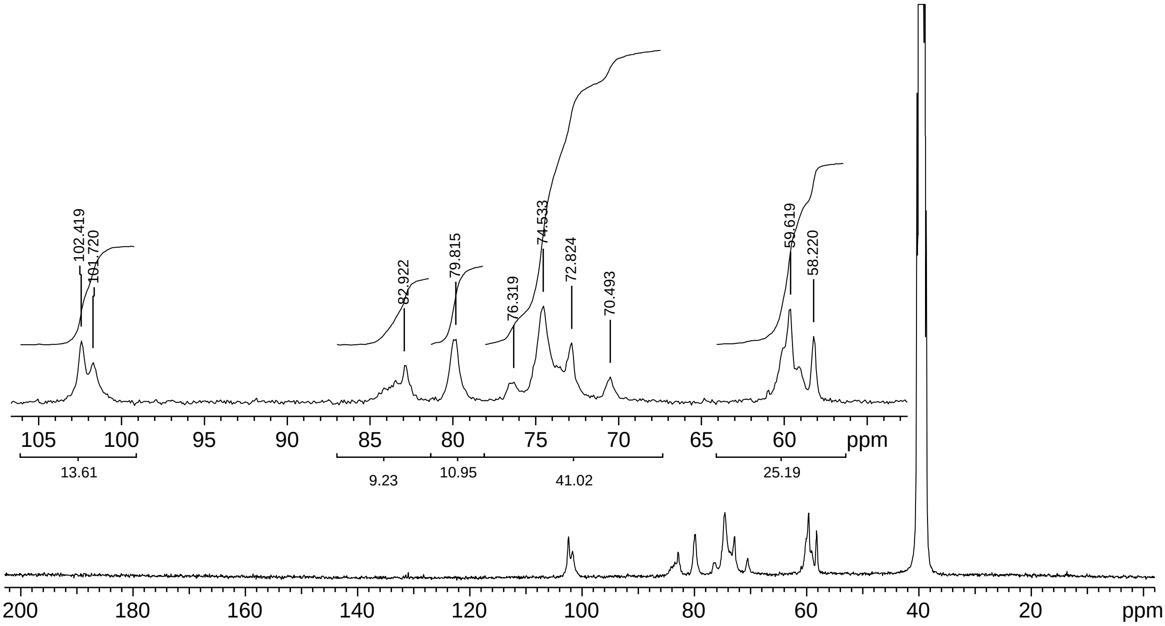

Fig. 1. The ^{13}C NMR spectrum of MD37.

increased from 20 to 30%, the residual NaOH increased by 46%. When the retention time increased from 1 to 2 h, the residual NaOH increased by 53%. Under the same impregnation conditions, the eucalyptus chips absorbed less alkali than the spring cardoon chips. This indicates that the spring cardoon chips were more porous than the eucalyptus chips, which also means that the pulping severities of cardoon should be lower than the pulping severities of eucalyptus. After impregnation, the liquid turned black. This may have been due to the preliminary delignification by the degradation and dissolution of lignin in the concentrated NaOH solution. The best impregnation condition for the spring cardoon chips may be a 30% sodium hydroxide solution under 15 bars pressure for 2 h at 55 °C.

3.3. Steam pulping

Because of its lower lignin content and more porous stalks, the spring cardoon was pulped with lower pulping severities than the juvenile eucalyptus. The parameters and results of the steam pulping are shown in Tables 3 and 4. The *p*-factors of the spring cardoon pulps were the same (2.96), though they were impregnated in different conditions. The cardoon pulps had a higher intrinsic viscosity when its chips were impregnated at a lower concentration of NaOH solution. When the impregnation time of the chips increased, the intrinsic viscosity of the cardoon pulps decreased. When the pulping severity of eucalyptus chips increased, the kappa number, yield, lignin content and intrinsic viscosity of the eucalyptus pulps decreased. The spring cardoon chips were subjected to less severe impregnation conditions and steam pulping, so their pulps had higher kappa numbers and lignin contents. The yields of the spring cardoon pulps were lower than the eucalyptus

Table 1
Compositions of spring cardoon and eucalyptus

Component	Spring cardoon (%)	Eucalyptus (%)
Ash	5.0	1.5
Water extractives	26.7	7.6
Organic extractives	5.1	0.5
Klason lignin	13.9	25.4
Holocellulose	48.3	71.0
α-Cellulose	24.0	48.6

Table 2
Parameters and results of impregnation

Material	AQ (%)	NaOH concentration (%)	Retention time (h)	Temperature (°C)	Residual alkali (%)[a]
Cardoon 1	0.1	20	2	55	32.5
Cardoon 2	0.1	30	1	55	31.1
Cardoon 3	0.1	30	1.5	55	34.2
Cardoon 4	0.1	30	2	55	47.6
Eucalyptus	0.1	30	2	55	43.7

[a] Based on the initial NaOH charge.

Table 3
Steam pulping results of spring cardoon

Material	*p*-factor	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g, 25 °C)
Cardoon 1	2.96	30.4	21.9	4.56	1287
Cardoon 2	2.96	30.9	25.1	4.64	1305
Cardoon 3	2.96	23.8	23.7	3.57	1163
Cardoon 4	2.96	28.6	24.7	4.29	1077

Table 4
Steam pulping results of eucalyptus

Material	Reaction time (min)	Temperature (°C)	P factor	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g, 25 °C)
Eucalyptus 2	16	180	3.56	7.5	33.5	1.13	728.2
Eucalyptus 3	8	180	3.26	8.3	39.7	1.25	1135.5
Eucalyptus 4	24	180	3.74	7.4	31.5	1.11	622.7
Eucalyptus 5	16	190	3.85	7.2	35.0	1.08	761.5
Eucalyptus 6	24	190	4.03	6.3	29.3	0.95	534.7

pulps. The intrinsic viscosities of the eucalyptus pulps were lower than those of the spring cardoon pulps because the eucalyptus chips were cooked at higher pulping severities.

3.4. Bleaching

Bleaching results of the pulps of the cardoon and eucalyptus are listed in Tables 5 and 6. The bleached pulps of the spring cardoon had higher kappa numbers than summer cardoon pulps. The spring cardoon pulps seemed to be more difficult to bleach than summer cardoon pulps. This may indicate that the harvesting time of cardoon was an important factor for its pulping and bleaching. The most interesting phenomena were the summer cardoon pulps, which could be bleached to the lowest kappa number although their chips were cooked at the lowest pulping severity and lowest *p*-factor. The leaves and capitula of summer cardoon stalks were eliminated before cooking. This indicated that the quality of the bleached pulps of the cardoon could be improved by removing the leaves and capitula. The eucalyptus pulps were more difficult to bleach than the cardoon pulps but their unbleached pulps had lower kappa numbers. The yields of the eucalyptus pulps were higher than those of the cardoon pulps. This may be because the cardoon pulp was easier to degrade than the eucalyptus pulp. The viscosities of the eucalyptus pulps were lower than those of the cardoon pulps. Both the eucalyptus and cardoon bleached pulps had very low lignin contents, which showed that most of the lignin was removed after TCF bleaching. The *p*-factor greatly influenced the properties of the bleached eucalyptus pulps. When the *p*-factor increased, the kappa number, the lignin content and the viscosity of the bleached pulp decreased. These results show that, for both cardoon and the eucalyptus chips, high-quality bleached pulps can be produced by a combination of the IRSP process and a proper TCF bleaching sequence.

3.5. Methylation

The yields of methylcellulose are listed in Table 7. We can see that the methylcellulose of the summer cardoon had lower water-soluble contents than the methylcellulose of the spring cardoon and eucalyptus. The eucalyptus methylcellulose had higher water-soluble contents than the cardoon methylcellulose. Most of the alkali soluble contents of methylcellulose were over 95%. The methylcellulose of the spring cardoon had the lowest alkali soluble contents of all the methylcellulose samples. It seems that the eucalyptus

Table 5
Bleaching results of cardoon pulps

Material	*p*-factor	Method	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g, 25 °C)
Cardoon 3	2.96	PP	11.3	80.3	1.70	678.4
Cardoon 4	2.96	PEP	4.5	59.8	0.68	605.6
Cardoon 5[a]	2.96	PP	2.1	84.9	0.32	729.6
Cardoon 6[a]	2.66	PP	3.5	74.8	0.53	720.4
Cardoon 7[a]	2.66	PP	1.4	76.6	0.21	636.6
Cardoon 8[a]	2.66	PP	1.4	78.5	0.21	643.2

[a] Pulp of summer cardoon.

Table 6
Bleaching results of eucalyptus pulps

Material	*p*-factor	Method	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g, 25 °C)
Eucalyptus 2	3.56	PP	4.5	94.1	0.77	423.8
Eucalyptus 3	3.26	PP	5.1	94.3	0.68	720.3
Eucalyptus 4	3.74	PP	3.9	97.1	0.59	361.3
Eucalyptus 5	3.85	PP	3.7	94.6	0.56	543.0
Eucalyptus 6	4.03	PP	2.5	94.6	0.38	399.6

Table 7
Yields of methylcellulose (MC)

Material	Methylcellulose	Alkali soluble MC (%)	Water-soluble MC (%)
Cardoon 1	MD27	74.36	66.83
Cardoon 2	MD28	86.66	81.52
Cardoon 3	MD20	98.56	62.59
Cardoon 4	MD30	92.24	27.02
Cardoon 5	MD31	96.69	15.20
Cardoon 6	MD32	96.36	7.10
Cardoon 7	MD33	99.85	15.96
Cardoon 8	MD34	98.21	23.25
Eucalyptus 2	MD35	96.77	82.14
Eucalyptus 3	MD36	93.62	59.59
Eucalyptus 4	MD37	98.40	82.82
Eucalyptus 5	MD38	97.07	81.84
Eucalyptus 6	MD39	98.11	83.49

pulps were easier to methylate with iodomethane. This may be because of the higher impregnation condition and pulping severities of the eucalyptus chips, which yielded pulps of looser and smaller microfibrils and lower molecular weights and degrees of polymerisation. When we compared these methylcellulose samples, we found that the lowest water-soluble content was prepared from the summer cardoon at the lowest pulping severity. This shows that the pulping condition is one of the main factors for the synthesis of methylcellulose.

The DS of methylcellulose are shown in Table 8. Most of spring cardoon methylcellulose had the biggest DS values. The spring cardoon pulps were subjected to higher pulping severities than the summer cardoon pulps. Higher pulping severities led to better pulp accessibility. Though the pulping severities of eucalyptus were higher than those of spring cardoon, the eucalyptus methylcellulose had lower DS. This shows that species is a deciding factor for the synthesis of methylcellulose, so cardoon pulps subjected to less severe pulping conditions may be better raw materials than eucalyptus if we only consider the DS value. Our data show that DS values in the second OH group were bigger than those in the third and sixth OH group. Methylation in the third and sixth OH group was more difficult. With the *p*-factor increased, total DS values and the DS values in the second OH group increased.

Table 8
DS of cardoon and eucalyptus methylcellulose

Material	Methyl-cellulose	DS at C2	DS at C3	DS at C6	Total DS
Cardoon 3	MD20	0.41	0.25	0.34	1.00
Cardoon 4	MD30	0.47	0.44	0.42	1.33
Cardoon 5	MD31	0.38	0.15	0.12	0.65
Cardoon 6	MD32	0.37	0.12	0.10	0.59
Cardoon 7	MD33	0.32	0.11	0.09	0.52
Cardoon 8	MD34	0.28	0.10	0.08	0.46
Eucalyptus 2	MD35	0.41	0.20	0.20	0.81
Eucalyptus 3	MD36	0.38	0.22	0.16	0.76
Eucalyptus 4	MD37	0.44	0.21	0.21	0.86
Eucalyptus 5	MD38	0.40	0.19	0.23	0.82
Eucalyptus 6	MD39	0.53	0.28	0.26	1.07

Table 9
Viscosities of cardoon methylcellulose

Material	Methylcellulose	0.5% in 4% NaOH (mPas, 20 °C)	1% in DMSO (mPas, 20 °C)
Cardoon 3	MD20	1.72	4.89
Cardoon 4	MD30	3.36	25.4
Cardoon 5	MD31	4.76	16.2
Cardoon 6	MD32	5.32	32.2
Cardoon 7	MD33	4.48	21
Cardoon 8	MD34	4.32	22.6

Table 10
Viscosities of eucalyptus methylcellulose

Material	Methylcellulose	0.5% in DMSO (mPas, 20 °C)	1% in 4% NaOH (mPas, 20 °C)
Eucalyptus 2	MD35	6.25	1.85
Eucalyptus 3	MD36	8.07	12.3
Eucalyptus 4	MD37	5.99	5.57
Eucalyptus 5	MD38	7.29	9.29
Eucalyptus 6	MD39	5.84	8.67

Viscosities in both DMSO and 4% NaOH solution are shown in Tables 9 and 10. Summer cardoon methylcellulose had higher viscosities than the spring cardoon methylcellulose in two solvents because the spring cardoon was subjected to higher pulping severities. When the *p*-factor increased, the viscosity of eucalyptus methylcellulose in DMSO and 4% NaOH solution decreased. This also shows that the *p*-factor is an important parameter for the synthesis of methylcellulose.

The intrinsic viscosities of the cardoon methylcellulose in the 4% NaOH solution are shown in Table 11 and the intrinsic viscosities of the eucalyptus methylcellulose are shown in Table 12. The summer and spring stalks could be

Table 11
Intrinsic viscosities of cardoon methylcellulose

Material	Methylcellulose	4% NaOH (ml/g, 20 °C)
Cardoon 3	MD20	175.6
Cardoon 4	MD30	340.3
Cardoon 5	MD31	227.4
Cardoon 6	MD32	379.4
Cardoon 7	MD33	369.4

Table 12
Intrinsic viscosities of eucalyptus methylcellulose

Material	Methylcellulose	DMSO (ml/g, 20 °C)	4% NaOH (ml/g, 20 °C)
Eucalyptus 2	MD35	110.6	65.7
Eucalyptus 3	MD36	242.4	182.6
Eucalyptus 4	MD37	97.1	58.8
Eucalyptus 5	MD38	176.9	104.9
Eucalyptus 6	MD39	87.5	69.4

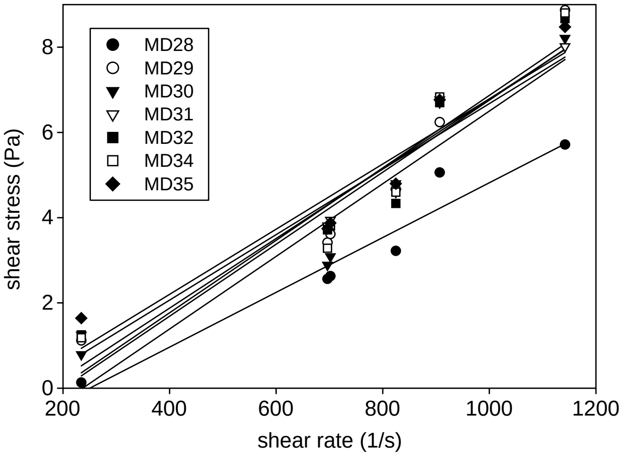

Fig. 2. Rheological property of 0.5% cardoon methylcellulose in 4% NaOH solutions.

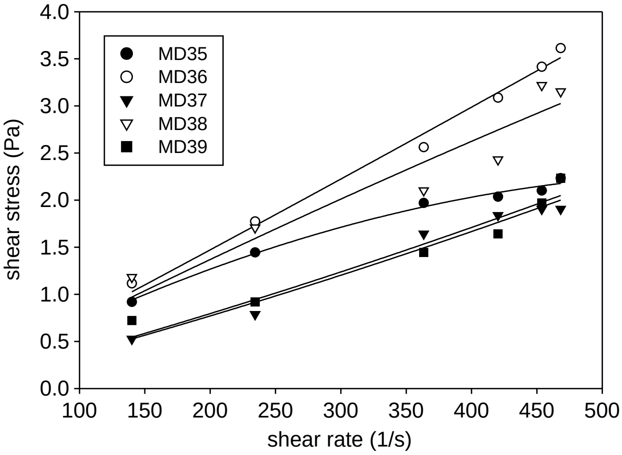

Fig. 4. Rheological property of 0.5% eucalyptus methylcellulose in DMSO solutions.

used to prepare methylcellulose with similar intrinsic viscosities, such as cardoon-4, cardoon-6, and cardoon-7. The eucalyptus methylcellulose had lower intrinsic viscosities than the cardoon methylcellulose, which may have been due to the higher pulping severity of the eucalyptus chips. The intrinsic viscosities in the DMSO solution were higher than those in the 4% NaOH solution.

The solution properties of the cardoon methylcellulose are shown in Figs. 2 and 3 and those of the eucalyptus methylcellulose are shown in Figs. 4 and 5. In DMSO all these figures had similar trends to those in the 4% NaOH solutions. All these curves seemed to increase linearly: shear stress values increased as shear rate values increased. All methylcellulose solutions were Newtonian solutions in two solvents. These curves were similar though they had different viscosities and substituted patterns (Figs. 1–5).

The application of methylcellulose prepared from cardoon and juvenile eucalyptus depends on the final objectives according to DS and viscosity. The prepared methylcellulose was crude-a mixture of alkali-soluble and water-soluble methylcellulose due to the heterogeneous methylation. For textile treatments, synthesised methylcellulose would need further purification with 4% NaOH solution to produce high-yield alkali-soluble methylcellulose. For aqueous applications, synthesised methylcellulose would need further purification with water to increase its DS and its solubility. Commercial methylcellulose is usually produced with a DS ranging from 1.4 to 1.9 and a viscosity ranging from 10 to 15,000 mPas of 2% aqueous solutions at 20 °C and 20 rpm (http://www.herc.com). Methylcellulose synthesised from cardoon had a DS ranging from 0.46 to 1.33 and intrinsic viscosities ranging from 176 to 379 ml/g. These DS and viscosities mean that methylcellulose synthesised from cardoon could be used as a viscosity controller. Methylcellulose synthesised from eucalyptus had a DS ranging from 0.76 to 1.07 and intrinsic viscosities ranging from 59 to 183 ml/g. These DS and viscosities mean that methylcellulose synthesised from eucalyptus could be used as a drug component or additives such as a low viscosity biopolymer (Kokubo et al., 1998).

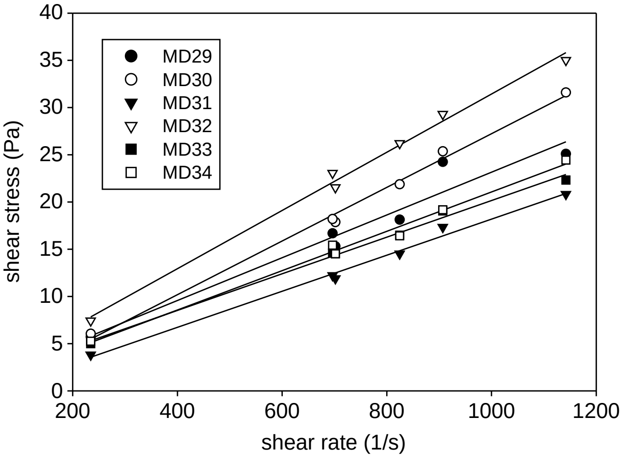

Fig. 3. Rheological property of 1% cardoon methylcellulose in DMSO solutions.

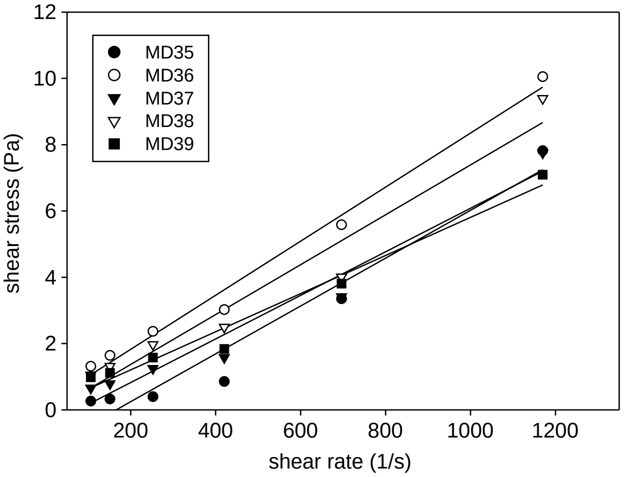

Fig. 5. Rheological property of 1% eucalyptus methylcellulose in 4% NaOH solutions.

3.6. Factors influencing the properties of methylcellulose

During impregnation, a longer retention time and a higher concentration of the NaOH solution showed that the pre-treatment had a beneficial effect on subsequent cooking. A longer retention time and a higher concentration led to a higher water soluble content, a higher DS value, a higher DS value at the second hydroxyl group, a higher DS value at the third hydroxyl group, a higher DS value at the sixth hydroxyl group, a higher viscosity in both DMSO and 4% NaOH solution, and a higher intrinsic viscosity in 4% NaOH solution.

During cooking, a higher *p*-factor demonstrated a better effect of defibrillation, removed more lignin and hemicellulose and created more voids in the microfibrils. Basically, a better cooked pulp led to a better accessibility and reactivity of the cellulose and, therefore, a better synthesised methylcellulose.

A plant species has an inherent fibre morphology and an inherent chemical composition. Inherent properties are essential factors to consider when preparing methylcellulose, not only in terms of the impregnation parameters but also in terms of the cooking variables. In this study, we therefore obtained different properties for the synthesised methylcellulose. Even with the same species, different harvest times influence the properties of synthesised methylcellulose. Different pulp accessibility and reactivity are therefore obtained by the same pulping and methylation methods. For different species, the parameters of impregnation, cooking, bleaching and even methylation need to be adjusted to obtain suitable properties for synthesised methylcellulose.

4. Conclusions

This study has demonstrated that the synthesis of methylcellulose from cardoon and juvenile eucalyptus is feasible and suitable. The methylcellulose samples prepared were a mixture of alkali methylcellulose and water-soluble methylcellulose. Solutions of methylcellulose in 4% NaOH solutions and DMSO were the Newtonian solutions. As the pulping severity increased, the DS and water-soluble contents increased and the intrinsic viscosities and solution viscosities decreased. Species may be a decisive factor for the synthesis of methylcellulose. We have also shown that pulping severity is an important factor for the preparation of methylcellulose. Cardoon can be used to produce higher viscosity methylcellulose, while juvenile eucalyptus can be used to produce lower viscosity methylcellulose.

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