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Preparation of Methylcellulose from Annual Plants

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By

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FAN CONSTAR

Que el present treball que porta per títol,

PREPARATION OF METHYLCELLULOSE FROM ANNUAL PLANTS

Que presenta el **DAIYONG YE** per optar al Grau de Doctor en Enginyeria Química, ha estat realitzat sota la nostra direcció en els laboratoris del Departament d’Enginyeria Química de la Universitat Rovira i Virgili, i que tots els resultats presentats i la seva anàlisis són fruit de la investigació realitzada per l’esmentat doctoranda.

I per què se’n pregui coneixement i tingui els efectes que correspongui signem aquesta certificació.

Tarragona, 16 de maig de 2005

Dr. Xavier Farriol Roigés
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Dedicated to my family:

To my father, Shifu Ye;

To my mother, Jingying Cheng;

To my wife, Miaoying Chen;

To my son, Peng Ye.

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Abstract

Preparation and characterization of methylcelluloses from some annual plants were investigated.

Miscanthus, cardoon, and eucalyptus pulps were produced by Impregnation Rapid Steam Pulping (IRSP) process and bleached by Total Chloride Free (TCF) sequences using hydrogen peroxide and sodium hydroxide. With an increase of pulping severities, accessibilities and reactivities of bleached pulps increased while viscosities and kappa numbers decreased. A novel facile methylation was developed in order to prepare methylcelluloses from wood and annual plants. Each methylcellulose of TCF bleached pulps was synthesized in isopropanol slurry with iodomethane at 60^0C for 22 hours after the TCF bleached pulp was mercerized in 40% NaOH solution for 1 hour. The mercerization and methylation were repeated in order to obtain a higher degree of substitution (DS). Fourier Transform Infrared (FTIR) spectra showed OH groups of cellulose were partially substituted by methoxyl groups. Supramolecular substitution patterns of methylcelluloses were determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Intrinsic viscosities of methylcelluloses were measured in distilled water, 4% NaOH solution, or dimethyl sulphoxide (DMSO). Rheological properties of methylcelluloses were measured in DMSO, 4% NaOH solution or distilled water, in which the synthesized methylcelluloses had similar properties as commercial methylcelluloses. Water-soluble and alkali-soluble contents of methylcelluloses were determined by solvent extraction.

We used iodomethane to synthesize methylcelluloses from Elemental Chloride Free (ECF) bleached abaca, hemp, flax, jute, and sisal pulps via heterogeneous and homogeneous methylations. The heterogeneous methylation was carried out in isopropanol with iodomethane at 60^0C for 22h after a ECF bleached pulp was mercerized in excessive 50% NaOH solution for one hour at ambient temperature. The homogeneous methylation was carried out in dimethyl sulfoxide with iodomethane at 30^0C for 48h using a methylcellulose of low degree of substitution. Fourier Transform Infrared (FTIR) spectra of the synthesized methylcelluloses showed the existence of methoxyl groups on methylcellulose molecules. The degrees of substitution of the synthesized methylcelluloses were measured by ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy. The molecular weights of the water-

soluble methylcelluloses were determined by Size Exclusion Chromatography (SEC). Intrinsic viscosities of the synthesized methylcelluloses were measured in 4% NaOH solution. Methylcelluloses with better properties, such as greater degrees of substitution, molecular weights, viscosities, and intrinsic viscosities, were prepared from the pulps with higher accessibilities and reactivities. The factors influencing the preparation of methylcelluloses from these pulps were discussed.

Pretreatments (water-soaking, pre-mercerization, mercerization under a pressure of 15 bars, and steam explosion) were used to improve the accessibilities and reactivities of celluloses of bleached flax, hemp, sisal, abaca, and jute pulps for the synthesis of methylcellulose. Glucose and xylose contents of these pulps were determined by High Performance Liquid Chromatograph (HPLC) after hydrolysis. Degrees of crystallinity of these pulps were determined by X-ray Diffraction (XRD) spectra. Figures of Scanning Electron Microscope (SEM) showed that their fibrils had different morphological structures. The iodine adsorption accessibilities of these pulps were low and accessible fractions ranged from 1.3% to 5.2%. Accessible fractions in amorphous cellulose were calculated in the 5% to 18% range. The accessibilities of these pulps were hemp pulp > flax pulp > sisal pulp > jute pulp > abaca pulp. Fourier Transform Infrared (FTIR) spectra showed that mean hydrogen bond strengths were weakened and relative crystallinity indexes were decreased by pretreatments. The accessibility and reactivity of the abaca pulp were improved by water soaking, mercerization under 15 bars pressure, steam explosion and preliminary mercerization, of which steam explosion and pre-mercerization were the best treatments. Species was the main factor for the accessibility and reactivity.

We studied the factors that influenced the molecular weights (Mw) of water-soluble methylcelluloses prepared from annual plants and juvenile eucalyptus. Miscanthus and cardoon stalks, and bleached pulps of abaca, jute, sisal, hemp, and flax were used as the annual plant materials. A higher concentration of NaOH solution during the impregnation led to a spring cardoon methylcellulose having a lower molecular weight. As the impregnation times increased, so did the molecular weights of the water-soluble methylcelluloses of spring cardoon. The impregnation conditions had less influence on the methylcelluloses of summer cardoon than on the methylcelluloses of spring cardoon. As the cooking times increased, so did the molecular weights of miscanthus methylcelluloses. A lower pulping severity increased the molecular weight of eucalyptus methylcellulose. The preliminary treatments (water soaking, pre-mercerization, mercerization under pressure and steam explosion) improved the molecular weights of water-soluble abaca

methylcelluloses. The steam explosion method was the best of the preliminary treatments for the abaca pulp. Different species led to different molecular weights for methylcelluloses synthesized from ECF bleached pulps, and these were further improved by preliminary mercerization. The molecular weight of α-cellulose methylcellulose changed as the ratio of the methylation reagent was varied. In order to synthesize an optimum Mw of methylcellulose, the different raw materials can be chosen, the pulping parameters adjusted (including impregnation and cooking), the cellulose pretreated, and the methylcellulose conditions changed. The plant species is the decisive factor for the Mw of methylcellulose.

The pulping parameters, the methylation conditions, the species, the pretreatments, and the morphological structures of pulps influenced the degrees of substitution of the methylcelluloses prepared from the annual plants. A higher impregnation severity, a higher pulping temperature, and a longer pulping time caused a higher degree of substitution. An increase of methylation reagents led to an increase of degree of substitution. Methylcelluloses of different degrees of substitution were synthesized from the pulps of different species when a same methylation condition was used. The pretreatments increased the degrees of substitution of methylcelluloses.

This investigation contributes to find appropriate conditions for the production of methylcellulose from annual plants. The present investigation demonstrates these annual plants have the capacities to produce upgraded and high quality methylcelluloses for varied applications, such as additives of foods, construction, pharmaceutics, polymerization, paints, and detergents etc. The industry can utilize these annual fast-growth plants to produce methylcelluloses. Therefore, a lot of wood will be saved.

Keywords: abaca, accessibility, annual plants, cardoon, degree of substitution, eucalyptus, flax, hemp, IRSP pulping, jute, methylation, methylcellulose, miscanthus, molecular weight, sisal, steam explosion, TCF bleaching.

Resumen

Este trabajo presenta los resultados de la investigación sobre la preparación y caracterización de las metilcelulosas a partir de las plantas anuales.

Las pastas del miscanthus, el cardo, y el eucalipto, se prepararon mediante el proceso IRSP (*Impregnation Rapid Steam Pulping*) y se blanquearon con las secuencias del TCF (*Total Chloride Free*), que usan peróxido de hidrógeno y hidróxido de sodio (NaOH). Con el aumento de la severidad del proceso de obtención de las pastas, la accesibilidad y la reactividad de las pastas aumentaron mientras que la viscosidad y el número de la *kappa* disminuyeron. Se desarrolló un nuevo y sencillo método de metilación para preparar las metilcelulosas a partir de la madera y las plantas anuales en el laboratorio. Cada metilcelulosa de las pastas blanqueadas con las secuencias del TCF se sintetizó en una mezcla de isopropanol con metano de yodo a 60^0C durante 22 horas después la pasta del TCF se mercerizó en una solución del hidróxido de sodio al 40% durante 1 hora. La mercerización y la metilación se repitieron para obtener un grado de sustitución (DS) más alto. Los resultados de la espectroscopía infrarroja de transformada de Fourier (FTIR) (*Fourier Transform Infrared Spectroscopy*) mostraron que los grupos del OH de la celulosa habían sido sustituidos parcialmente por grupos del metoxil. Los modelos de sustitución supramolecular de las metilcelulosas se determinaron mediante espectroscopía de resonancia magnética nuclear del carbono-13. La viscosidad intrínseca de las metilcelulosas se midió con agua destilada, una solución al 4% de NaOH, o DMSO. Las propiedades reológicas de las metilcelulosas se midieron con DMSO, una solución al 4% de NaOH o agua destilada. Las metilcelulosas sintetizadas tenían unas propiedades similares a las metilcelulosas comerciales. Los volúmenes hidrosolubles y alcalinosolubles de la metilcelulosas se determinaron mediante extracción con disolventes.

Las metilcelulosas se prepararon a partir de pastas de lino, yute, cáñamo, sisal, y abacá mediante metilaciones heterogéneas y homogéneas. Estas pastas se blanquearon mediante el proceso ECF (*Elemental Chlorine Free*). La metilación inhomogénea de las pastas blanqueadas mediante el proceso ECF se sintetizó en una mezcla de isopropanol con metano de yodo a 60^0C durante 22 horas después la pasta del ECF se mercerizó durante 1 hora en una solución de NaOH al 50%. La

metilación homogénea de la pasta blanqueada mediante ECF se realizó en DMSO con metano de yodo a 30^0C durante 48 horas. Para esta metilación homogénea se usó una metilcelulosa con un grado de sustitución más bajo, que se disolvió completamente en DMSO. La espectroscopía infrarroja de transformada de Fourier (FTIR) de las metilcelulosas mostró la existencia de grupos de metoxiles sobre las moléculas de metilcelulosa. Se utilizó la espectroscopia de resonancia magnética nuclear del carbono 13 para medir los grados de sustitución de las metilcelulosas. Los pesos moleculares de las metilcelulosas hidrosolubles se determinaron con la cromotagrafía de exclusión por tamaños (SEC). Las viscosidades intrínsecas se midieron en una solución de NaOH al 4%. Las metilcelulosas preparadas a partir de pastas de elevadas accesibilidades y reactividades tenían las mejores grados de sustitución, pesos moleculares, viscosidades y viscosidades intrínsecas

Se investigaron las accesibilidades y reactividades de las pastas del ECF. Los volúmenes de glucosa y de xilosa de estas pastas se determinaron mediante HPLC (*High performance liquid chromatography*) después de la hidrólisis. Las accesibilidades de adsorción de yodo de estas pastas eran bajas y sus fragmentos accesibles estaban entre el 1,31% y el 5,16%. En la región amorfa, sus fragmentos accesibles estaban entre el 5% y el 24%. Las imágenes del SEM (*Scanning Electron Microscopy*) mostraron que sus fibrillas tenían distintas estructuras morfológicas. Los resultados de la espectroscopía infrarroja de transformada de Fourier (FTIR) mostraron que, después de los pretratamientos, habían disminuido tanto la media de la intensidad de los enlaces de hidrógeno como los índices de cristalinidad relativos. Sus reactividades aumentaron significativamente después de la mercerización preliminar. Las accesibilidades y reactividades de la pasta del abacá se mejoraron con los tratamientos de impregnación con agua, la mercerización a 15 bares de presión, la explosión de vapor y la mercerización preliminar. La desintegración, el incremento de los huecos, el debilitamiento de la intensidad de los enlaces de hidrógeno, la depolimerización, y la decristalización son esenciales para mejorar las accesibilidades y las reactividades, pero el factor decisivo es la especie de la planta.

Hemos estudiado los factores que influyen en el peso molecular (Mw) de las metilcelulosas hidrosolubles preparadas a partir de plantas anuales. El tiempo y la temperatura de impregnación y las condiciones de cocción influyeron de manera diferente en el peso molecular (Mw) de metilcelulosas preparadas a partir de los cardos recogidos en primavera y en verano, el miscanthus y el eucalipto. Se compararon los efectos de los pretratamientos (la impregnación con agua, la mercerización preliminar, la mercerización con presión y la explosión de vapor) en la

pasta del abacá. Cuando se pretrató la pasta del abacá, su metilcelulosa hidrosoluble consiguió un peso molecular más alto. De entre los pretratramientos analizados, la explosión de vapor resultó el más adecuado. Para conseguir metilcelulosas con un peso molecular más alto deben perfeccionarse las condiciones de la preparación de las pastas blanqueadas mediante ECF. La especie de las plantas es el factor decisivo para conseguir el peso molecular más alto de las metilcelulosas y para seleccionar los pretratamientos más adecuados.

Los parámetros del proceso de obtención de pastas, las condiciones de la metilación, las especies de las plantas, los pretratamientos, y la estructura morfológicas de las pastas influyó en los grados de sustitución de las metilcelulosas preparadas a partir de plantas anuales. Una severidad de impregnación más alta, una temperatura del proceso de obtención de pastas más alta y un incremento del tiempo del mismo proceso consiguieron grados de sustitución más altos. Un aumento de reactivos de la metilación causó un aumento de grado de sustitución. Las pastas obtenidas de distintas especies produjeron grados de sustitución diferentes, trabajando con las mismas condiciones de metilación. Los pretratamientos aumentaron el grado de sustitución de las metilcelulosas.

Esta investigación contribuye a encontrar las condiciones apropiadas para metilcelulosas diseñadas a medida, sintetizadas a partir de plantas anuales. Esta investigación demuestra que estas plantas tienen la capacidad de ser preparadas para conseguir metilcelulosas de alta calidad y de alto valor aptas para distintas aplicaciones, como la industria alimentaria, la de la construcción o la farmaceútica. La industria puede utilizar estas plantas anuales de crecimiento rápido para producir metilcelulosas, con lo que, además, se evitará el uso de madera.

Palabras clave: abacá, accessibilidad, blanqueo mediante TCF, cáñamo, cardo, eucalipto, grado de sustitución, lino, metilación, metilcelulosa, miscanthus, peso molecular, plantas anuales, proceso de obtención de pasta IRSP, sisal, yute.

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Nomenclature

AGU	Anhydrous Glucose Unit
APMP	Alkaline Peroxide Mechanical Pulping
AQ	Anthraquinone
ASAM	Alkaline Sulfite Anthraquinone Methanol
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflection
CMC	Carboxymethyl Cellulose
CTMP	Chemi-Thermomechanical
DMAc	Dimethyl Acetamide
DMSO	Dimethyl Sulfoxide
DP	Degree of Polymerization
DS	Degree of Substitution
DSC	Differential Scanning Calorimetry
ECF	Elementary Chorine Free
FAO	Food and Agriculture Organization
FTIR	Fourier Transform Infrared Spectroscopy
HPLC	High Performance Liquid Chromatography
IDE	Impregnation Depolymerization Extraction
IRSP	Impregnation Rapid Steam Pulping
ISO	International Standards Organization
MC	Methylcellulose
NMR	Nuclear Magnetic Resonance
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
TAPPI	Technical Association of the Pulp and Paper Industry (USA)
TCF	Totally Chlorine Free
THF	Tetrahydrofuran
XRD	X-Ray Diffraction

1. Introduction

1.1. Introduction

1.1.1. Annual plants

The total global production of paper and paperboard increased from 268,515,320 metric tons in year 1994 to 328,065,011 metric tons in year 2004 (FAOSTAT data, 2004), in which wood is the dominant resource. Combining overproduction of agricultural crops and shortage of wood, non-wood materials, such as annual plants and agricultural residues, receive more attention in recent years for produce of pulp, paper, paperboard, and cellulose derivatives. In fact, non-wood materials had been used to produce cellulosic products since the invention of papermaking by a Chinese, Cai Lun (Atchison and McGoven, 1987).

Wood is not available in sufficient quantities in many countries because of the increasing consumption of furniture, construction, paper, paperboard, and cellulose derivatives (Atchison, 1996; McCloskey, 1995; Nick and Emmanuel, 2000). Alternative new non-wood raw materials need to be investigated and exploited for the potential substitution of wood. Therefore, the cellulose industry is investigating such new resources as overproduced crops, agricultural waste, unconventional plants and common wild plants to decide whether it is feasible to use them to produce paper, paperboard and cellulose derivatives, such as tailor-designed methylcellulose as an additive for cement, food and drug.

Annual plants are considered as potential resources because of overproduction of agricultural crops (Pande, 1998; Hon, 2000), their higher yield of cellulose than wood (McDougall et al., 1993; Atchison, 1996; Han, 1998), lower lignin contents and consumption of less pulping chemicals and energy (McDougall et al., 1993; Han and Rowell, 1996; Oggiano et al., 1997). Annual plants have same main chemical components as woody plants, i.e., cellulose, hemicellulose, lignin, and extractives. Annual plants have less lignin contents and looser fibril structure than wood. Thus, cellulose can be obtained from them by a mild pulping process, which consumes less energy and chemicals in a shorter cooking time (Patt et al., 1986). The investment on producing processes reduces at the same time. Annual plants can be planted, cultivated, and harvested every year. These special characters were the dominant direct importance for their development.

However, the annual plants have some specific problems as raw materials of cellulosic products (Patt et al., 1986). Harvesting is limited to only a few weeks of a year. Annual plants are planted and scattered in many small fields that thus cause the difficulty of transportation and collection. A sufficient store capacity is needed to set up to ensure an all-year supply. Most annual plants are attacked easily by microorganisms (Patt et al., 1986). To minimize degradation, these plants should be stored as dry as possible.

Transportation of wood was more expensive and difficult than annual plant (McDougall et al., 1993; Ilvessalo-Pfäffi, 1995). Under the consideration of the economical objective, the environment influence, the sufficient supply, and the higher yield of cellulose, annual plants are now gradually substituting woods as alternative resources of cellulosic products.

1.1.1.1. Miscanthus, cardoon, and eucalyptus

Miscanthus sinensis (elephant grass) was introduced into Europe from China and Japan as an ornamental plant during the 1930s. Miscanthus 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). It has been reported to yield between 20-26 dry tons per hectare, depending on the condition of the soil. This 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). Investigations have shown that miscanthus sinensis is a promising source of pulp in the Mediterranean area (Iglesias et al., 1996; Oggiano et al., 1997). It has been shown to be an effective bioenergy crop and a high-quality source of paper (Oggiano et al., 1997; Iglesias et al., 1996; Fukuda and Hishikawa, 1996; Barba et al., 2002). Nowadays, miscanthus’ innovative investigations concentrate on achieving higher yield, better selectivity, and improved quality with sulphur-free pulping technologies, chlorine-free bleaching, and new applications.

Annual cardoon (Cynara cardunculus) is an herbaceous perennial plant belonging to the Compositae family (Antunes et al., 2000; Gominho et al., 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 (Pereira et al., 1994; Dalianis et al., 1996; Antunes et al., 2000; Gominho et al., 2001). Its average production is 20 tons/ha per year, with about 40% stalks, 25% leaves, and 35% capitula (Fernandez, 1992; Fernandez and Curt, 1995). In recent years, cardoon has been shown to be a potential pulping and energy resource in southern Europe (Dalians et al., 1994; Pereira et al., 1994; Fernandez and Curt, 1995; Benjelloun et al., 1998; Antunes et al., 2000; Piscioneri et al., 2000; Gominho et al., 2001).

Cardoon is perfectly adapted to Spain’s continental conditions (Dalians et al., 1994; Pereira et al., 1994; Fernandez and Curt, 1995; Benjelloun et al., 1998; Antunes et al., 2000; Piscioneri et al., 2000; Gominho et al., 2001). The Spanish government plans to promote renewable energy, so they are promoting a plantation of 1 million hectares 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 Hectares of eucalyptus are planted in over 70 counties (Davidson, 1993; Montagu et al., 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 and Emmanuel, 2000). Pulps or cellulose made from a young two-year-old eucalyptus improve land utilization and produce higher cellulose yields than a usual eucalyptus of several years.

Higher valued methylcelluloses, which were produced from the annual miscanthus, the juvenile eucalyptus of two years and the annual cardoon planted in marginal and set-aside lands, of course will upgrade the low-grade plants and improve the utilization of lands (Fernandez, 1992; Fernandez and Curt, 1995; http://www.nf-2000.org). In this dissertation, three new challenging materials, the annual miscanthus, the annual cardoon (harvested both in spring and in summer) and the juvenile eucalyptus, would be exploited and evaluated their feasibility for the production of methylcelluloses, which were for the first time to be investigated.

1.1.1.2. Five commercial pulps of annual plants

We used five commercial pulps of abaca, flax, hemp, jute, and sisal. These five annual plants can be used to produce methylcelluloses (Ye and Farriol, 2005b). Annual plants can be used to produce methylcellulose, though the quality depends strongly on the source (Modrzejewski and Kieruczenkowa 1950; Ye and Farriol 2005a, b). The cellulose contents of abaca (56-63%), sisal (47-62%), hemp (57-77%), flax (43-47%) and jute (45-63%) are higher than that of woods (38-49%) (Han and Rowell 1996). The lignin contents of abaca (7-9%), sisal (7-9%), hemp (9-13%), flax (21-23%) and jute (21-26%) are lower than that of woods (23-34%) (Han and Rowell 1996). The high cellulose content and low lignin content make these annual plants valuable for producing cellulosic products (Han and Rowell 1996). As Table 1 and Table 2 (http://www.fao.org, 2004) shows, the good yields and stable productions of these annual plants in recent years make it feasible to try to exploit them as alternative new resources of methylcelluloses.

Table 1. World production of some annual plants (Metric tons)

Year	1999	2000	2001	2002	2003	2004
Jute	2592893	2662360	2929993	2861483	2749747	2773642
Flax	474179	479135	610697	762161	748369	750640
Sisal	353891	413050	305177	287142	301367	306667
Abaca	99840	104430	98320	100230	100230	100230
Hemp	61140	50618	62917	74054	83290	83290

Table 2. Yield of some annual plants (Hg/Ha)

Year	1998	1999	2000	2001	2002	2003	2004
Jute	18165	19070	19369	20420	20221	20664	20256
Hemp	11629	10168	8674	9874	10985	12357	12357
Sisal	8053	9514	10944	8180	8345	8387	8352
Flax	8716	9854	10954	11985	16436	15603	15667
Abaca	7728	7598	8233	7705	7769	7769	7769

In this dissertation, five commercial dissolving pulps (abaca, flax, hemp, jute, and sisal) were used to prepare methylcelluloses. The synthesis would concentrate on the accessibilities and reactivities of ECF bleached pulps. Different pretreatment methods would be used to improve the properties of the synthesized methylcelluloses. The main properties of the synthesized methylcelluloses would be characterized: alkali-soluble and water-soluble contents, DS and DS distribution along the glucose units, degrees of polymerization and molecular weights, rheology and solubility in water and 4% NaOH solution. Both the pulp species and the pretreatment methods would be compared.

1.1.2. Methylcellulose

Methylcellulose is one of important cellulose ethers (Nikitin, 1962; Greminger, 1979; Brandt, 1986; Just and Majewicz, 1985; Hon and Shiraishi, 1991; Donges, 1990; Krassig, 1993; Coffey and Bell, 1995). Methylcellulose has very wide applications (Donges, 1990; Greenway, 1994; Coffey and Bell, 1995; Guo et al., 1998). Building industry uses about 47% of worldwide produced methylcellulose (about 70000 t/y) (Greminger, 1979; Greminger and Krumel, 1981; Donges, 1990; Greenway, 1994). Paints, wallpaper paste, cosmetics and pharmacy, detergents and polymerization industry consume about 21%, 14%, 4% and 5% of methylcelluloses, respectively (Donges, 1990). Methylcellulose is used as a surfactant because of the presence of both hydrophilic OH and hydrophobic OCH_3 groups on its chains (Brandt, 1986). Cement and gypsum formulations, water-based paints, and wallpaper adhesives use methylcellulose because of its excellent water retention properties (Brandt, 1986). Methylcellulose is used as a drug to treat eye illness. Methylcellulose is used as an additive of drugs, food and cosmetics, in which methylcellulose functions as a component of coating, a drug release controller, a viscosity controller, a filler of tablet and capsule etc (Donges, 1990; Greenway, 1994; Coffey and Bell, 1995; Guo et al., 1998).

Suida synthesized methylcellulose for the first time (Suida, 1905; Croon and Manley, 1963). Methylcellulose is synthesized by the Williamson etherification with iodomethane, methyl chloride, or dimethyl sulfate (Nikitin, 1962; Greminger, 1979; Fengel and Wegener, 1984; Brandt, 1986; Just and Majewica, 1985; Donges, 1990; Brandt, 1986). Commercially produced methylcelluloses have two types: (1) water-soluble methylcelluloses with degrees of substitution (DS) ranging from 1.4 to 2.0 (usually 1.8), (2) alkali-soluble methylcelluloses with degrees of substitution (DS) ranging from 0.25 to 1.0 (Brandt, 1986). Methylcellulose is made in different viscosities ranging from 4 to 100,000 mPas in 2% aqueous solution at 20^0C with 20rpm. Methylcelluloses of different DS and viscosity satisfy their diverse applications.

Mercerization of dissolving pulp with a concentrated NaOH solution causes the cellulose to swell, to degrade, to decrease the degree of crystallinity, and, the most important, to yield the alkali cellulose, which reacts with methyl halide to produce methylcellulose. The reaction of alkali cellulose and methyl halide is carried out as a nucleophilic substitution through the interaction of the oxonium sodium hydroxide complexes on three accessible hydroxyls of the anhydroglucose unit (Krässig, 1993). When the bleached pulp is used to synthesize methylcellulose rather than the pure cellulose, the William etherification mechanism, combined with the macro heterogeneous methylation of pulp (Timell and Purves, 1951; Rebenfeld, 1954), causes the methylation to become more inhomogeneous and incomplete because of the difficulty of reagent diffusion, competitive reactions of lignin and hemicellulose, the inaccessible fibril interiors, and the crystalline cellulose interiors (Rebenfeld, 1954; Krässig, 1993). Synthesized methylcellulose is often comprised of un-reacted fibrils, methylcellulose with an inhomogeneous distribution of the methoxyl group, and salts.

Currently, the synthesis of methylcellulose focuses on the essential properties: the degree of substitution, the molecular weight (or the degree of polymerization), and the distribution of the methoxyl group along both the anhydroglucose unit and the methylcellulose molecule chain. The methylcellulose can be dissolved in cold water when the degree of substitution is between 1.3 and 2.0 (Croon and Manley, 1963). For a given degree of substitution, the molecular weight is the deciding factor of methylcellulose for its solubility and application (Timell and Purves, 1951). Properties such as the number average molecular weight, the weight average molecular weight, the polydispersity, and the degree of polymerization constitute the essential characteristics for the optimal synthesis and application of water-soluble methylcellulose.

Methylcelluloses of viscosities higher than 50,000 mPas in 2 % aqueous solution at ambient temperature are produced from cotton linters because cotton has a degree of polymerization as high as 10,000 (Brandt, 1986). Methylcelluloses of lower viscosities are produced from sulfite-processed wood pulps (Brandt, 1986). The pulps for production of methylcelluloses are required as almost free of lignin, highly purified and high α-cellulose contents of more than 86 % (Brandt, 1986). Sulfate-processed wood pulps are less used (Brandt, 1986). Methylcelluloses can also be produced from annual plant pulps (Ye and Farriol, 2003).

The molecular weight of methylcellulose needs to be kept within a particular range by carefully choosing the raw materials and process parameters. In the present research, methylcellulose was prepared from plant stalks and bleached pulps. The experimental process consisted of impregnation, pulping, bleaching, mercerization, and methylation. Pulps of different plants have different morphological structures and chemical compositions (Hon and Rowell, 1996), so the methylcellulose produced from different species will have different properties even though the methylation conditions may be the same (Ye and Farriol, 2005b). Therefore, the species is the most important factor in the production of methylcellulose (Ye and Farriol, 2005b). Pulping conditions played a very important role in adjusting the properties of the pulp (e.g. the lignin content, the degree of polymerization, the accessibility, and the degree of crystallinity) (Fengel and Wegener, 1984; Ye and Farriol, 2005a). In addition, bleached pulps often have different chemical and physical compositions (Ye and Farriol, 2005b), which determine whether the pulp needs preliminary treatments for its accessibility and reactivity to be improved (Krassig, 1993; Ye and Farriol, 2005b). When the accessibility of pulp is low, the pulp needs physical and chemical preliminary treatments (Krassig, 1993; Ye and Farriol, 2005b). During the heterogeneous methylation, the mercerization and methylation conditions also greatly influence the molecular weight of the synthesized methylcellulose (Brandt, 1986; Krassig, 1993).

1.2. Objective

The object of this dissertation is to exploit the studied annual plants as new alternative resources for the production of methylcelluloses. In this dissertation, methylcelluloses were prepared from miscanthus, cardoon, eucalyptus, flax, hemp, jute, sisal, and abaca. The parameters of preparation, and the resulting intermediate products as well as the final products, methylcelluloses, were characterized and compared at each experimental step. The present research concentrated on the conditions of preparation (pulping, bleaching and methylation) and the factors that influenced the main properties of methylcelluloses (viscosities, intrinsic viscosities, molecular weights, and degrees of substitution etc.). Experiments were done according to the following six steps.

1. Impregnation;
2. Rapid steam pulping;
3. TCF bleaching;
4. Improving accessibility and reactivity of bleached pulps;
5. Methylation of TCF and ECF bleached pulps;
6. Characterization of synthesized methylcelluloses.

1.3. Organization of the dissertation

This dissertation has five important chapters. Each chapter explains a specific topic of the present investigation.

The chapter 1 is a short introduction, which briefly describes the studied raw materials, investigated topics, and the objective of this dissertation.

The chapter 2 is a literature review about the fundamental knowledge, the progress and current development of the topic that is investigating in this dissertation. This chapter begins with a review on the importance of the annual plants, their compositions and fiber morphology, the pulping and bleaching processes that are suitable for annual plants, and finally cellulose derivatives including celluloses esters, cellulose ethers, and the most important methylcellulose in this dissertation. In this chapter, the synthesis, main characteristics, and applications of methylcellulose are emphasized and described.

The chapter 3 is an experimental process part, which in details describes the materials, equipment, procedures to prepare methylcelluloses, separation and purification, and characterization methods that use the current advanced technologies.

The chapter 4 describes the obtained experimental data, the interpretation of these dada, and comparison of obtained results with pertinent reference data. This chapter is the most important in this dissertation. This chapter consists of seven important sections.

(1) The first section is a short introduction, which emphasizes the originality, and the innovative points of the present investigation in this dissertation.

(2) The second section describes the development of a novel facile methylation method, which is suitable for annual plants and woods in laboratories.

(3) The third section describes the preparation and characterization of methylcelluloses from miscanthus, cardoon, and eucalyptus. This section includes the following parts: chemical composition, impregnation, steam pulping, TCF bleaching, methylation of miscanthus pulps, and methylation of cardoon and eucalyptus pulps. The potential applications of synthesized methylcelluloses are discussed.

(4) The fourth section describes the preparation and characterization of methylcelluloses from the commercial ECF bleached abaca, flax, hemp, jute and sisal pulps. This section includes three parts: properties of pulps, accessibilities and reactivities of pulps, and preparation and characterization of the synthesized methylcelluloses.

(5) The fifth section describes the factors that influence the molecular weights of methylcelluloses: pulping conditions, pretreatments, methylation conditions, harvest time, and species.

(6) The sixth section describes the factors that influence the degrees of substitution of methylcelluloses: pulping conditions, pretreatments, methylation conditions, and species.

(7) The seventh section discusses the course of methylation of bleached pulps,

which includes mercerization, methylation, effect of the bleached pulps, and finally the factors that influence the properties of methylcelluloses.

Based on the results described in the chapter 4, the chapter 5 is a summary of the most important conclusions.

Finally, the chapter 6 lists cited references.

2. Literature review

2.1. Introduction

In recent years, natural lignocellulosic resources have been investigated as alternative raw materials for energy and chemicals. This is mainly because of the limited reserves of petroleum and coal, the high price of natural gas (Lee, 2004) and the need for sustainable development (Hartley, 1990; Dincer, 2000). Since 1983, several potential industrial woods and annual herbs, such as eucalyptus, willow, miscanthus, cardoon, flax, and jute, have been investigated in European countries for energy and chemical production (Mangan, 1995).

Lignocellulosic materials can partially substitute fossil resources for producing energy (Hartley, 1990) and chemicals (Goldstein, 1978 a and b, 1980; Koukios catalytic steam reformation, chemical or enzymatic hydrolysis, fermentation (Linko, 1987) or other chemical, biological and physical reactions (Saddler and Mackie, 1990). The main components of lignocellulosic materials are cellulose, hemicellulose, and lignin. Many higher value-added products that have been produced from cellulose, lignin, and hemicellulose have diverse applications (Koukios and Valkanas, 1982).

Currently, about 55% of the feedstock for the production of pulps is virgin wood, 9% is non-woody sources, and 16% is recycled paper (FAOSTAT data, 2004). The main woods for cellulosic products are from rapid growth species such as eucalyptus and pine. Agricultural crops (especially straws and bagasse) and natural plants can be alternative sources to forest woods if they can be found in sufficient supply, in a proper plantation area and with suitable technology for obtaining the cellulose. Other lignocellulosic residual resources have not yet been well exploited. These are industrial residues (wastes from the production of pulp and lumber), forest residues, agricultural residues (residues of fruits, cereals, textile fibers and excess production of crops), and urban residues (waste paper, paperboard and similar materials) (Barba, 2002).

The most important annual plants for the pulp industry are agricultural residues (bagasse and cereal straws) and naturally cultivated bamboo and reeds (Patt et al., 1986). Other important annual plants, such as miscanthus, flax, kenaf, sisal, jute, hemp, and cotton, are valuable raw materials for the production of special pulps, special papers, and cellulose derivatives (Patt et al., 1986; Ye et al., 2003; Ye and Farriol, 2005b).

2.2. Annual plants

Annual plants are an opportunity both for agricultural farmers and cellulosic industries (Foeher, 1998). Cellulose has been produced from annual plants for a long time (Marshak, 1933; Orlov, 1934; Jayme et al., 1948). About 8% of the world's cellulosic products are made from annual plant resources (Leminen et al., 1996).

Plant species used for cellulosic products are from the botanical division *Spermatophyte* (seed plants), which has two classes: *Angiospermae* (seeds enclosed within the fruit) and *Gymnosperm* (naked seeds) (Nimz et al., 1986). *Gymnosperm* has *Coniferae* (Figure 1). *Angiospermae* has two classes: *Monocotyledon* and *Dicotyledon* (Figure 1). The most common plant species used for cellulosic products are coniferous trees (softwood trees) of the *Gymnosperm* and deciduous trees (hardwood trees) of the *Dicotyledon*. Grasses and leaf fiber plants are examples of *Monocotyledon* (Nimz et al., 1986). Bast and fruit fiber plants are examples of *Dicotyledon* (Nimz et al., 1986).

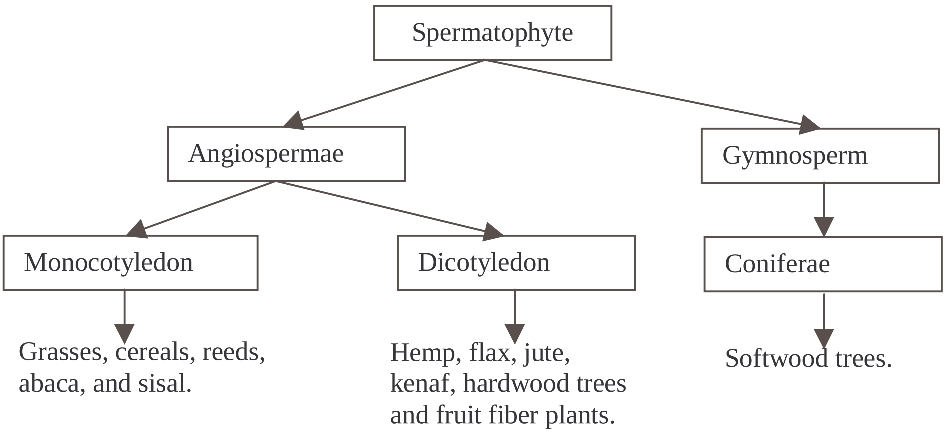

Figure 1. The taxonomy of lignocellulosic plants (Ilvessalo-Pfaffli, 1995)

Annual plants have several advantages over wood resources. Firstly, they grow to maturity much more quickly than wood species. Hemp can be harvested within three to four months. Other annual plants such as straw, flax, abaca etc. can be harvested yearly. This brings quicker profits for the farmers and obtains a higher cellulose yield. Secondly, crop residual fibers such as bagasse, straw, flax, jute, and wild plants can be used, so profits are higher profit thanks to these low-value lignocellulosic sources. Thirdly, annual plant sources are usually chipped to smaller sizes (about 4 cm in length) than wood chips in the pulp digester. Annual plant stalks have more porous fiber structures and weaker inter-fiber lignin deposits (Brandt, 1986). This requires less cooking energy and less time. Bagasse and straw, for example, cooks within 10 to 15 minutes, which save a lot of energy in a short time. Finally, fewer cooking and bleaching chemicals are used for annual plants than for wood chips (Brandt, 1986).

Annual plants generally have lower lignin contents, higher pentosan contents, higher hemicellulose contents, and higher ash contents (especially silica) than woods, while the cellulose contents are almost equivalent (Atchison and McGovern, 1987; Han and Rowell, 1986). So far these plants have only been used the manufacture of textiles and paper products that constantly compete with synthetic and wood fibers (Brandt, 1986). The feasibility of using annual plant fibers in other applications has not been widely researched or developed (Valadez et al., 1999; Idarraga et al., 1999; Beard et al., 2002a). The most widely available annual plants are the straws of cereals, the stems of corn and sugar cane, which are listed in Table 3 (Atchison, 1994) and Table 4 (FAOSTAT, 2004).

Table 3. Worldwide availability of annual plant fibers*

Fiber Type	Potential Availability for Pulping (Million BDMT)**
Agricultural Residues	
Wheat Straw	600.0
Other Cereal Straws	290.0
- Barley Straw	195.0
- Oat straw	55.0
- Rye straw	40.0
- Rice straw	360.0
Grass Seed Straw	3.0
Seed Flax Straw	2.0
Corn Stalks	750.0
Sorghum Stalks	252.0
Cotton Fibers	89.0
- Cotton Staple Fiber	18.3
- Cotton Linters (First and Second Cut)	2.7
- Cotton Stalks	68.0
Sugar Cane Bagasse	102.2
Nonwoody Crop Fibers	
Stem Fibers	13.9
- Jute, Kenaf, Hemp, etc.	
Leaf Fibers	0.6
- Sisal, Henequen, Maguey, Abaca	
Natural Growing Plants	
Reeds (Estimate)	30.0
Bamboo (Estimate)	30.0
Papyrus (Estimate)	5.0
Esparto Grass (Estimate)	0.5
Sabai Grass	0.2

*: Source: Atchison J. and McGovern J., 1987.

**: Fibers available for delivery to pulp mills. Bone Dry Metric Ton (BDMT).

The jute has a wider plantation area and greater production than the other most cultivated annual plants, such as flax, sisal, ramie, abaca, and hemp (Table 4, FAOSTAT data, 2004). Table 4 shows the supply of these annual plants for cellulosic products. The research and development of methylcelluloses from these plants will therefore be both significant and feasible. Some annual plants, such as miscanthus, hemp, and kenaf, have higher fiber and pulp yields than straws of wheat and rice, which are shown in Table 5 (Pierce, 1991). Land can therefore be better utilized by planting fast-growing annual plants. These data highlight the need to exploit these annual plants for the production of methylcellulose.

Table 4. Worldwide plantation of some annual plants in 2004*

	Area (Ha)	Yield (Hg/Ha)	Production (Mt)
Jute	1,369,311	20,256	2,773,642
Flax Fiber and Tow	479,115	15,667	750,640
Jute-Like Fibers	315,340	12,840	404,883
Sisal	367,178	8,352	306,667
Ramie	128,600	20,941	269,300
Abaca	129,020	7,769	100,230
Hemp Fiber and Tow	67,404	12,357	83,290

*: Source: FAOSTAT data, 2004

Table 5. Average annual yields of some raw materials*

Plant	Fiber yield (Tonnes/year/ha)	Pulp yield (Tonnes/year/ha)
Scandinavian softwood	1.5	0.7
Fast-growing softwood	8.6	4
Temperate softwood	3.4	1.7
Fast-growing hardwood	15	7.4
Wheat straw	4	1.9
Rice straw	3	1.2
Bagasse	9	4.2
Bamboo	4	1.6
Kenaf	15	6.5
Hemp	15	6.7
Miscanthus	12	5.7
Canary grass	8	4.0

*: Source: Pierce, 1991.

2.2.1. Chemistry of annual plants

2.2.1.1. Chemical components of annual plants

The dry cell walls of annual plants mainly consist of cellulose, hemicellulose, and lignin combined with extractives, protein, starch, and lower quantities of inorganics (Han and Rowell, 1996). The chemical composition varies from species to species, and within different parts of the same species (Han and Rowell, 1996). It also varies within a species from different geographic plantation locations, ages, climate, and soil conditions (Han and Rowell, 1996). If they are exploited appropriately, they can be used in the research and development of cellulose and cellulose derivatives with innovative properties and diverse applications (Maddern and French, 1995).

The cellulose contents of annual plants range from 43% to 90 % (Table 7). This is highly variable and greater than that of softwood trees. The lignin contents of annual plants range from 7 to 24 %, which is much lower than that of woods (23–39 %) (see Table 7). Less energy and less chemical consumption will therefore be expected during the production of cellulose from annual plants. The hemicellulose contents of annual plants range from 15 to 32 %, which is much higher than that of woods (7–26%) (see Table 7). The smallest components of annual plants are extractives and inorganics, which are usually less than 10% of the total weight of the dry fibers.

Cellulose

Cellulose, the chemical formula of which is $(C_6H_{10}O_5)_n$, is an unbranched homopolymer consisting of β-D-glucopyranose units linked by $(1\rightarrow4)$ glycosidic bonds (Purves, 1954). As the main component of renewable photosynthesized biomass, cellulose is the most abundant biopolymer available in wood, annual plants and other minor resources (Krässig, 1993). 10^{11}–10^{12} tons of cellulose is photosynthesized annually (Krässig, 1993). ^{1}H NMR spectroscopy showed that the β-D-glucopyranose adopts the $^4C_1$ chain conformation, which is the lowest free energy conformation of the molecule (Krassig, 1993). Thus, the hydroxyl groups are arranged in the ring plane (equatorial), while the hydrogen atoms are in the vertical position (axial) (Krassig, 1993). Each glucose unit of cellulose has three hydroxyl groups at the C-2, C-3, and C-6 atoms, which combine with the oxygen atoms of both the pyranose ring and the glycosidic bond to form strong inter- and intra-hydrogen bonds (Sarko, 1978; OSullivan, 1997). The number of glucose units in a cellulose molecule is referred to as the degree of polymerization (DP). The average DP of plant celluloses, which depends not only on the species but also on the process used, ranges from about 50 for a sulfite pulp to about 10,000 for cotton (Stamm, 1964).

Cellulose is a biopolymer of glucose (Krässig, 1993). The structure of glucose is shown in Figure 2. Two glucose molecules react to form a cellobiose (Figure 3), which is the basic chemical unit of a cellulose molecule (Figure 4) (Krässig, 1993).

Figure 2. Glucose

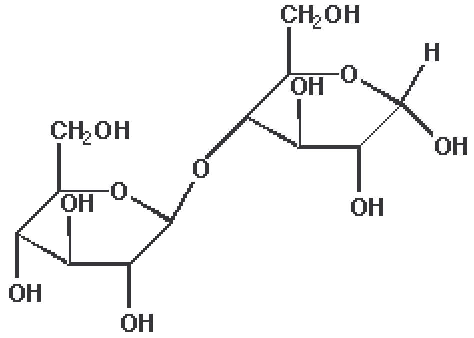

Figure 3. Cellobiose

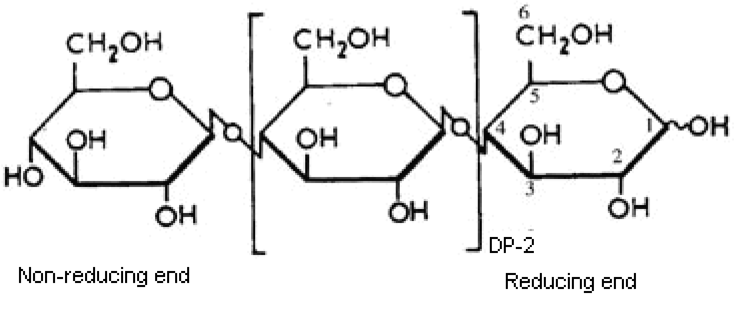

Figure 4. Structure of a cellulose chain

Hydrogen bonds of cellulose

Both intra- and intermolecular hydrogen bonds exist in cellulose. This causes the crystalline cellulose, a different morphology of cellulose, and an assembly of elementary fibrils (Krässig, 1993). The hydrogen bonds between O-3-H and O-5’ of the adjacent glucopyranose unit and O-2-H and O-6’ in native crystalline cellulose (Figure 5) can be observed by X-ray diffraction, NMR, and IR spectroscopic data (Liang and Marchessault, 1959; Krässig, 1993; Sarko and Muggli, 1974). The intramolecular hydrogen bonds are highly related with the single-chain conformation and stiffness of cellulose (Krässig, 1993). The intermolecular hydrogen bonds are highly related with the crystallinity and morphology of cellulose (Sarko, 1978; Osullivan, 1997). The intermolecular hydrogen bonds between the OH group at the adjacent C-6 and C-3 positions of cellulose molecules are located on the same lattice plane (020 planes) (Osullivan, 1997).

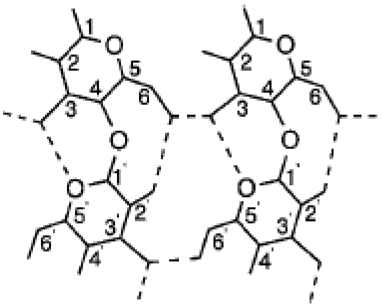

Figure 5. The hydrogen bonds of cellulose

Crystallinity of cellulose

Because of the strong hydrogen bonds and weak van de Wall’s forces, the celluloses are in fact a mixture of amorphous and crystalline celluloses (Meyer and Mark, 1928; Meyer and Misch, 1937). The species and process determine the ratio of amorphous cellulose to crystalline cellulose, or the degree of crystallinity (Fink et al., 1995). About 93% of Valonia is crystalline cellulose: 600–1000 parallel chains may exist in a microfibril of Valonia (Osullivan, 1997). Bacterial cellulose has a degree of crystallinity of about 75% (Kulshreshta and Dweltz, 1973) and a crystallite width of about 5-6 nm. Cotton has a degree of crystallinity of 40–45% and a crystallite width of 4-5 nm (Morosoff, 1974). The density of crystalline cellulose in a single crystal is 1.59 g/cm^3. In contrast, the density of pure natural fiber cellulose is only 1.55 g/cm^3 (Hermans, 1949).

Model of cellulose

Several models have been proposed to explain the structure of cellulose (Osullivan, 1997). Because of strong hydrogen bonds and a weak van de Wall's force, adjacent cellulose chains form elementary fibrils with an average thickness of 3.5 nm that contain both crystalline and amorphous molecules (Frengel, 1971). The elementary fibrils are cellulose aggregates of various lengths and widths that depend on the source and processes (Figure 7) (Osullivan, 1997). Hemicelluloses are enclosed in the elementary fibrils or exist between the elementary fibrils. The hemicelluloses form a looser structure than the elementary fibrils (Frengel, 1971). According to Fengel and Wegener (1989), several elementary fibrils with hemicellulose can associate with one another to form microfibrils, which also have diverse lengths and widths (Frengel, 1971). Several microfibrils are held together to form fibrils about 30 nm wide, which are enclosed in a matrix of hemicellulose and lignin (Figure 9) (Fengel and Wegener, 1989). The dimensions of these models are described in detail in the following paragraphs and figures (Osullivan, 1997).

(1) Cellulose macromolecules (Figure 6)

The distance between individual glucose molecules is about 6 angstroms and the distance between individual chains is about 5.4 angstroms (Fengel and Wegener, 1989).

(2) Elementary fibrils (Figure 7)

An elementary fibril is the basic unit of cellulose, which is about 30 x 30 angstroms in cross section and about 300 angstroms in length (Fengel and Wegener, 1989; Osullivan, 1997).

(3) Microfibrils (Figure 8)

A microfibril is approximately 120 x 120 angstroms in cross section and an indefinite length, and is composed of a bundle of elementary fibrils (Fengel and

Wegener, 1989; Osullivan, 1997). When viewed in cross-section, its appearance is much like that of the fibril.

(4) Fibrils (Figure 9)

A fibril is composed of bundles of microfibrils (Fengel and Wegener, 1989; Osullivan, 1997). It is approximately 2000 angstroms in width (Fengel and Wegener, 1989; Osullivan, 1997). Fibrils are of indefinite lengths. When viewed in cross-section, they appear as organized blocks within a matrix of hemicelluloses and lignin (Fengel and Wegener, 1989; Osullivan, 1997).

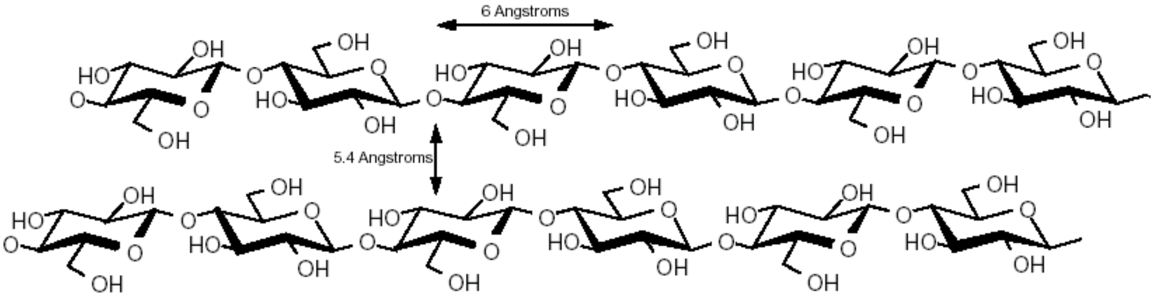

Figure 6. Cellulose macromolecule

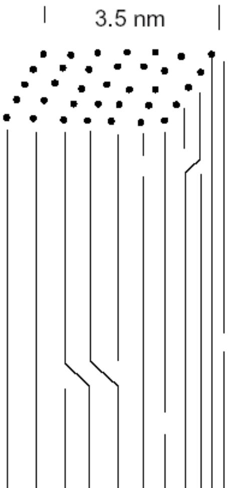

Figure 7. An elementary fibril (Osullivan, 1997)

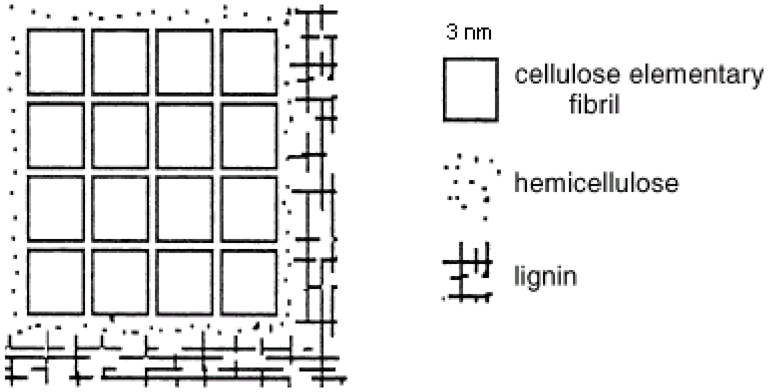

Figure 8. A microfibril with hemicellulose and lignin (Osullivan, 1997)

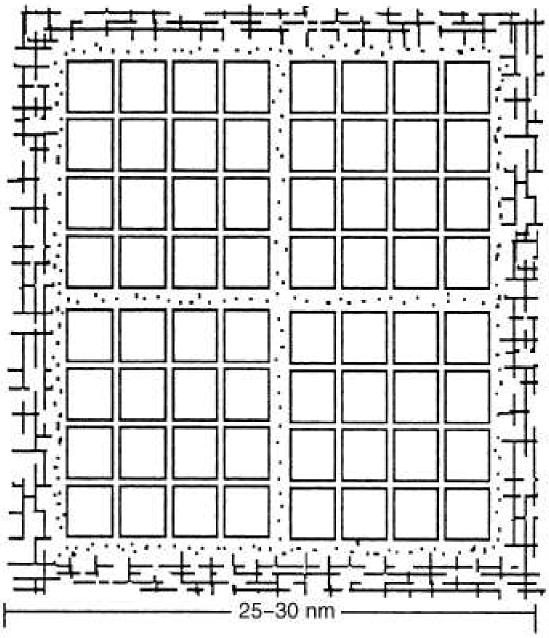

Figure 9. A fibril model (Osullivan, 1997)

lignin

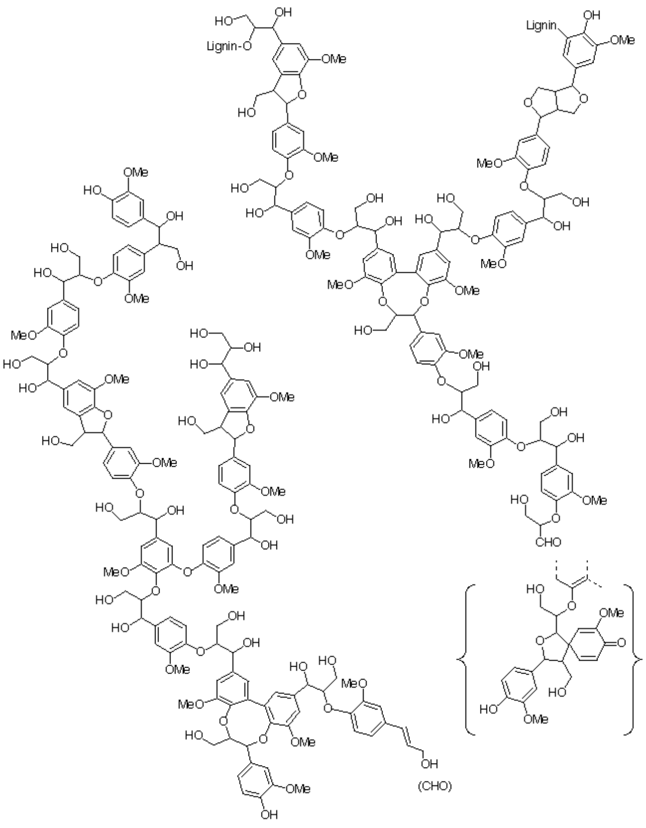

Figure 10. Brunow's softwood lignin model (Brunow, 2001)

Lignins (Figure 10) are cross-linked amorphous aromatic polymers of phenylpropane units (Sjöström, 1981). All plant lignins consist mainly of three basic building blocks of guaiacyl, syringyl, and *p* –hydroxyphenyl moieties, although other aromatic type units also exist in many different types of plants (Sjöström, 1981). Structures of lignins vary a lot within different plant species. Lignins in plants contain significant amounts of constituents other than guaiacyl- and syringyl-propane units (Sarkanen and Ludwig, 1971). Coniferous wood lignin consists mainly of guaiacylpropane (4-hydroxy-3-methoxyphenylpropane) units (Sjöström, 1981). Deciduous wood lignins contain more than 50 % of syringyl (3,5-dimethoxy-4-hydroxyphenyl) groups (Sjöström, 1981). Grass lignins contain more than 30 % of phydroxyphenylpropane (Sjöström, 1981). Corn lignin contains vanillin and syringaldehyde units along with substantial amounts of *p* -hydroxybenzaldehyde (Sjöström, 1981). Bamboo lignin is a mixed dehydration polymer of coniferyl, sinapyl, and *p* -coumaryl alcohols (Bhargava, 1987). Kenaf lignin contains a very high amount of syringyl groups (Han and Rowell, 1996).

Hemicelluloses

Hemicelluloses are amorphous polysaccharides of lower molecular polymers, which have degrees of polymerization (DP) of 50–200 (Sjöström, 1981). Hemicelluloses mainly contain D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, and D-glucopyranosyluronic acid with minor quantities of other sugars (Figure 11) (Han and Rowell, 1996). Bamboo hemicelluloses consist of a backbone polymer of D-xylopyranose, linked β-(l–4) with an average of every eight-xylose-unit containing a side chain of D-glucuronic acid attached glycosidically to the 2-position of the xylose sugar (Bhargava, 1987). Kenaf hemicelluloses contain a backbone polymer of D-xylopyranose with side chains of D-galactose and L-arabinose (Cunningham et al., 1987).

Galactoglucomannan is the main hemicellulose (about 20%), with a linear or possibly slightly branched chain with β- (1–4) linkages (Sjöström, 1981), in which glucose and mannose make up the backbone polymer with branches containing galactose. Another major hemicellulose in softwoods (5-10%) is an arabinoglucuronoxylan consisting of a backbone of β- (1–4) xylopyranose units with (l–2) branches of D-glucopyranosyluronic acid on the average of every 2–10 xylose units and the (l–3) branches of L-arabinofuranose on the average of every 1.3 xylose units (Sjöström, 1981). The major hemicellulose (glucuronoxylans) from hardwoods contains a backbone of D-xylose units linked β- (1–4) with acetyl groups at C-2 or C-3 of the xylose units, on an average of 7 acetyls per 10 xylose units (Sjöström, 1981). The xylan is substituted with side chains of 4 -*O*- methylglucuronic acid units linked to the xylan backbone through a link (l–2) with an average frequency of approximately 1 uronic acid group per 10 xylose units (Sjöström, 1981). Hardwoods also contain 2–5% of a glucomannan composed of β-D-glucopyranose and β-D-mannopyranose units linked (1–4) (Sjöström, 1981). The major hemicellulose from kenaf is similar to a hardwood xylan (Duckart et al., 1988). The major hemicellulose from bamboo is composed of a backbone of β- (14) D-xylopyranose residues whose every eighth xylose unit on average contains a side chain of D-glucuronic acid attached glycosidically to the 2-position of the xylose unit (Bhargave, 1987). Table 6 shows the sugar unit compositions of several annual plants (Han and Rowell, 1996). The composition of these plants is highly variable and xylose is the main sugar unit in the hemicellulose.

Table 6. Carbohydrate composition of some annual plants*

Fiber	Glucose	Arabinose	Galactose	Rhamnose	Xylose	Mamnose
Jute core	39.09	0.11	0.41	0.38	17.35	0.91
Flax	31.21	1.17	1.77	0.62	12.29	1.13
Rice hull	33.89	1.52	0.85	0.05	13.95	0.16
Bagasse	43.10	1.93	0.55	0	24.19	0.18
Kenaf core	33.45	0.49	0.83	0.29	14.24	1.01
Jute fiber	56.87	0.11	0.49	0.16	12.17	0.50
Abaca	52.69	1.83	1.03	0.16	12.81	0.89
Kenaf	43.32	2.04	0.46	1.25	10.80	1.25
Chinese hemp	0.40	83.81	1.34	2.11	0.79	1.92
Sunn hemp core	0	41.46	0.26	0.73	0.27	17.08
Sunn hemp bast	0.23	56.38	1.08	2.05	0.29	1.97

*: Source: Han and Rowell, 1996.

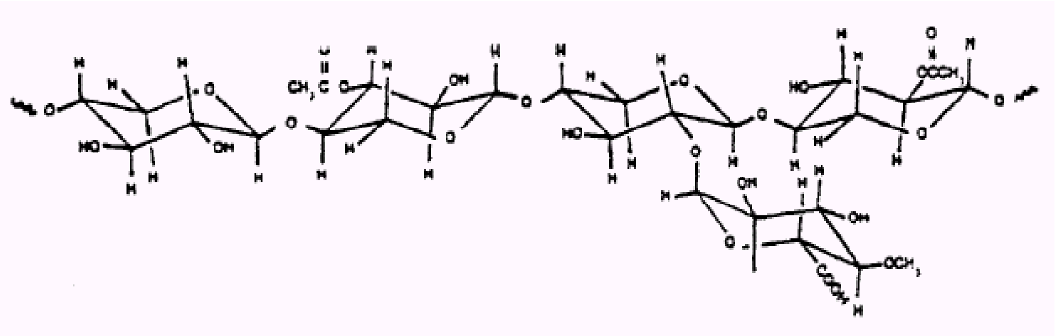

Figure 11. Partial structure of glucuronoxylan (Han and Rowell, 1996)

Extractives

Annual plants contain 1–10 % extractives (Han and Rowell, 1996). Higher contents of extractives have been found in certain types of cardoon with green stalks (Ye et al., 2005a). The extractives consist of a large number of low molecular weight compounds, which can be extracted from annual plants with organic solvents (terpenes, fats, waxes, and phenols) or water (tannins and inorganic salts). The extractives are chemicals mainly consisting of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, etc., which exist as monomers, dimers and polymers (Han and Rowell, 1996).

Inorganics

The inorganic content of a plant is usually referred to as its ash content, which is an approximate measure of the mineral salts and other inorganic matter in the fiber (Han and Rowell, 1996). Annual plants contain 1–10 % ash, which are mostly mineral components (Han and Rowell, 1996). Well-cleaned annual plants usually have a much greater silica component than wood, which causes problems during pulping and papermaking (Patt et al., 1986). The mineral components are mainly carbonates or glucuronates of calcium (40 - 70 %), potassium (10 - 30 %), magnesium (5 - 10 %), iron (up to 10 %) and sodium. Other metals, such as manganese and aluminum, are also present in smaller quantities (Han and Rowell, 1996). Oxalate, phosphate, and silicate anions also exist (Han and Rowell, 1996).

2.2.1.2. Chemical compositions of annual plants

The chemical compositions of annual fibers vary greatly, not only according to their species, plantation location, and growth environment but also to their harvest times (Han and Rowell, 1996). Studies have reported many varieties in fiber sources, fiber ages, and determination methods (Han and Rowell, 1996). Data on the chemical composition of several common plant fibers are shown in Table 7 (Han and Rowell, 1996). Generally, about 40 to 50% of the weight of annual plants is cellulose (which is the main component of these plants), except for cotton, which has a much higher cellulose content. About 10 to 30% of the weight of annual plants is lignin and 20 to

30% is hemicellulose. The ash content varies greatly. Annual plants have a much higher ash content than woods (Han, 1998).

The chemical compositions in Table 7 show that all annual plants have similar chemical properties, such as lower lignin contents, higher pentosan or hemicellulose contents and higher ash contents than woods. The chemical properties of stalk fibers are similar to those of hardwoods. The main difference is that these annual plants have higher ash and silica contents. Leaf and bast fibers usually have higher cellulose contents, lower lignin contents and higher pentosan contents than stalk fibers. Oilseed flax bast fiber has similar chemical properties to those of hardwoods. Cotton contains very pure cellulose, which is suitable for producing highly viscous cellulose derivatives.

Table 7. Chemical composition of natural fibers*

Fiber source		Cellulose (%)	α-cellulose (%)	Lignin (%)	Pentosans (%)	Ash (%)	Silica (%)
Leaf fibers							
Abaca			56-63	7-9	15-17	1-3	<1
Sisal		55-73	43-56	8-9	21-24	0.6-1	<1
Bast fibers							
Ramie		87-91			5-8		
Hemp		57-77		9-13	14-14	0.8	
Jute		45-63	39-42	21-26	18-21	0.5-1	<1
Kenaf (bast)		47-57	31-39	15-18	21-23	2-5	
Kenaf (core)			34	17.5	19.3	2.5	
Oilseed flax		43-47	31-39	21-23	24-26	2-5	
Textile flax		76-79	50-68	10-15	6-17	2-5	<1
Seed hull fibers							
Cotton			85-96	0.7-1.6		0.8-2	<1
Stalk fibers							
Canes	Bagasse	49-62	32-48	19-24	27-32	1.5-5	0.7-3.5
	Bamboo	57-66	26-43	21-31	15-26	1.7-5	0.7
Cereal straw	Barley	47-48	31-34	14-15	24-29	5-7	3-6
	Oat	44-53	31-37	16-19	27-38	6-8	4-7
	Rice	43-49	28-36	12-16	23-28	15-20	9-14
	Rye	50-54	33-35	16-19	27-30	2-5	0.5-4
	Wheat	49-54	29-35	16-21	26-32	4-9	3-7
Grasses	Arundo donax		29-33	21	28-32	4-6	1.1-1.3
	Esparto	50-54	33-38	17-19	27-32	6-8	2-3
	Sabai			22	24	6	
	Switchgrass		43	34-36	22-24	1.5-2	
Reeds	Phragmites comminis		44-46	22-24	20	3	2
Wood							
Coniferous		53-62	40-45	26-34	7-14	1	<1
Deciduous		54-61	38-49	23-30	19-26	1	<1

*: Source: Han and Rowell, 1996.

2.2.2. Morphological structure

Unlike wood fibers, which take years to grow to full size, most common annual plant fibers are harvested yearly and the entire plant grows within a very short time. Plant species, climate, soil conditions, and farming activities influence the fibers. Softwoods contain over 90% tracheid fibers, and only 10% stubby ray cells and other fines (Patt et al., 1986). Hardwoods contain only about 50% tracheid fibers and a large number of vessel cells and ray cells (Patt et al., 1986). Annual plants contain various fibers and cell types (Han and Rowell, 1996). Monocots such as cereal straws, sugarcane bagasse and corn stalks are similar to hardwoods but they are much more heterogeneous and contain a large proportion of thin-walled cells, barrel-shaped parenchyma cells, and vessel and fine epidermal cells in a wide range of dimensions (Han and Rowell, 1996). Dicots such as flax straw, kenaf, and hemp contain two different fiber types: an inner core of short fibers surrounded by a layer of longer bast fibers (Han and Rowell, 1996). Core fibers typically contain more lignin and are more difficult to pulp (Han and Rowell, 1996).

The morphological characteristics of fibers, such as length and diameter, are important for the manufacture of cellulosic products. In fibers for paper production, the ratio of fiber length to fiber diameter is about 100:1, whereas in textile fibers it is more than 1000:1 (Hurter, 1988; Hunsigi, 1989; McDougall et al., 1993). In coniferous trees, this ratio is 60–100:1, and in deciduous trees, it is 2–60:1 (Hurter, 1988; Hunsigi, 1989; McDougall et al., 1993). The fiber length and diameter of annual plants depends on the species and part of the plant from which the fiber is obtained (Han and Rowell, 1996). The average annual plant fiber length ranges from 1 to 30 mm (Table 8) (Hurter, 1988). The average ratio of fiber length to fiber diameter ranges from 50:1 to 1500:1 (see Table 8) (Hurter, 1988).

The average dimensions of various annual plant pulp fibers are listed in Table 8 (Atchison and McGovern, 1993). These data show the wide range of characteristics of annual plant fibers. Many annual plant fibers are similar to the short fiber hardwoods, while others are so long that they must be shortened to produce paper. These fiber dimensions provide an idea of the potential usefulness of these pulps in pulp and papermaking as well as cellulose derivation, where fiber morphology influences accessibility and reactivity. In fact, from the technical and quality viewpoints, any grade of cellulose derivatives can be produced from annual plants if the proper processes and technologies are used.

Table 8. Fiber dimensions of some plants*

Fiber source		Length (microns)			Diameter (microns)			L/D ration
		Maximum	Minimum	Average	Maximum	Minimum	Average	
Bast fibers								
Hemp		55000	5000	20000	50	16	22	1000
Jute		5000	500	2000	68	8	20	100
Kenaf (bast)		7600	980	2740			20	135
Oilseed flax tow		45000	10000	27000	30	16	22	1250
Textile flax tow		55000	16000	28000	28	14	21	1350
Core fibers								
Kenaf (core)		1100	400	600	37	18	30	20
Leaf fibers								
Abaca		12000	2000	6000	36	12	20	300
Sisal		6000	1500	3030			17	180
Seed hull fibers								
Cotton staple		50000	20000	30000	30	12	20	1500
Cotton linters		6000	2000	3500	27	17	21	165
Stalk fibers								
Canes	Bagasse	2800	800	1700	34	10	20	85
	Bamboo	3500-9000	375-2500	1360-4030	25-55	3-18	8-30	135-175
Cereal straw	Wheat mixed	3120	680	1480	24	7	13	110
	rice	3480	650	1410	14	5	8	175
Grasses	Esparto	1600	600	1100	14	4	9	120
	Lemon			1320			9	145
	Sabai	4900	450	2080	28	4	9	230
	Switchgrass			1370			12.5	110
Reeds	Arundo donax			1180			15	78
	Papyrus	8000	300	1500	25	5	12	125
	Phragmites comminis	3000	100	1500	37	6	20	75
Stalks	Corn	2800	680	1260	20	10	16	80
	Cotton	2000	700	860			19	45
Woods								
Coniferous		3600	2700	3000	43	32	30	100
Deciduous		1800	1000	1250	50	20	25	50

*: Source: Hurter, 1988.

2.3. Pulping of annual plants

The cellulose derivatives industry use exclusively cotton and wood pulps. Currently only about 8% of annual plant fibers is used for cellulosic products. Their use for such products is only growing in countries where wood resources are limited and annual plants are sufficiently available (Han and Rowell, 1996).

Pulping is the most common way to obtain cellulose from wood and annual plants. Pulping is a process of delignification, whereby lignin is partially eliminated, and a process of defibrillation, whereby aggregated fibrils are disintegrated. Pulp is actually a collection of the cellulosic fibers, which are liberated from the plant material, and contains less lignin and hemicellulose (Biermann, 1993). The fibers in the plant material are separated by physiochemical treatments with alkali, sulphite, or organic solvents, which partly eliminate the lignin and other non-cellulose components. Further processes, such as washing and screening, improve the quality and homogeneity of the pulps.

The pulping process comprises several stages (Singh, 1979; Fengel and Wegener, 1984; Garcia et al., 1984). These are pretreatment of raw materials, cooking (pulping), washing, and screening. Since annual plants have similar chemical components and morphological fiber structures to those of wood, wood most pulping processes can be used. The pulping of annual plants uses a lower temperature, a shorter cooking time, less chemical charge and, of course, less energy as well as newer pulping technologies. For the dissolving pulping process, pre-hydrolysis is often used to eliminate hemicellulose. For the production of cellulose derivatives, the pulping conditions should be modified to suit the specifications of the final cellulose required (molecular weight, purity, ash content, lignin content, residual hemicellulose content, etc.) (Casey, 1990; Kokurek et al., 1989; Abdul-Karim et al., 1994; Hinck et al., 1995).

2.3.1. Pretreatment of annual plants

The fibers of annual plants contain more dust, dirt, and leaves than those of wood. Annual plants must be thoroughly cleaned before cooking in order to remove adhering soil and other impurities. For material with a high pith content, especially sugarcane, a pith removal process must be carried out because parenchyma pith cells are unsuitable for subsequent use (Paavilainen, 1998). The material is usually chopped in a chipper to lengths of about 4 cm (Paavilainen, 1998). In the pulp mill, leaves, dust, and dirt can be removed by air fractionation before cooking. Fractionalization produces a chip fraction mainly of internodes for pulp production, and another fraction of leaves and sheaths, which can be used in the production of bioenergy (Paavilainen, 1998). Because of the large number of fines (small particles other than fibers), the dewatering ability of annual plant pulps is inferior to that of wood pulps (Patt et al., 1986; Wisur et al., 1993; Paavilainen, 1998), so drainage time is longer. The quality of pulps is improved by partially eliminating silica and other useless particles in the fibers.

2.3.2. Pulping processes

There are many pulping processes (see Table 9). These include mechanical pulping, semi-mechanical pulping, chemical pulping, and biopulping (Fengel and Wegener, 1984). The pulping processes suitable for annual plants are listed in Table 10. The most common commercial method for annual plant pulping is the soda method (Sadawarte, 1995). There are also several new physiochemical methods (Table 10) with good potential for producing high quality pulp from annual plants (McDougall et al., 1993). The kraft and neutral sulfite processes are less used. The acid sulfite process is not used because it produces brittle pulps with high ash contents and inadequate strengths (Patt et al., 1986). For higher yield pulping, the chemi-refiner mechanical pulping process is used. Mechanical pulps are suitable for newspaper but not for cellulose derivatives, which need celluloses of high purity to ensure high quality (Brandt et al., 1986).

The pulping processes concentrate not only on optimizing pulp quality but also on improving pulp yields, reducing energy consumption, reducing chemical consumption (and improving the recovery processes of the chemicals), reducing pollution and developing sulfur-free pulping processes and chlorine-free bleaching sequences (Fengel and Wegener, 1984).

Table 9. Pulping processes and yields*

Pulping process	Chemical treatment	Mechanical treatment	Plant**	Yield (%)
Mechanical pulping				
Stone groundwood	None	Grindstone	S	93–99
Steamed groundwood	Steam	Grindstone	S	80–90
Refiner mechanical	None	Disc refiner	A, S	93–98
Thermomechanical	Steam	Disc refiner (Pressure)	A, S	91–98
Asplund	Steam	Disc refiner	A, S	80–90
Biopulping	White rot fungi	Disc refiner	A, H, S	
	Ceriporiopsis subvermispora	Disc refiner	A, H, S	
Chemimechanical and Chem-thermomechanical pulping				
Chemigroundwood	Neutral sulfite	Grindstone	H, S	80–92
	Or Acidic sulfite		H, S	80–90
	or Na_2S + NaOH		H, S	85–90
Chemi-refiner mechanical pulp	NaOH or $NaHSO_3$ or Alkaline sulfite or Acidic sulfite	Disk refiner	A, H, S	80–90
Chemi-thermomechanical pulp	Steam + Na_2SO_3 + NaOH	Disc refiner (pressure)	A, H, S	65–97
Semimechanical pulping				
Neutral sulfite	Na_2SO_3 + Na_2CO_3 or $NaHCO_3$	Disk refiner	A, H	65–90
Cold soda	NaOH	Disk refiner	A, H	65–90
Alkaline sulfite	Na_2CO_3, Na_2S, Na_2OH	Disk refiner	A, H, S	65–90
Sulfate	Na_2S + Na_2OH	Disk refiner	A, H	65–90
Soda	NaOH	Disk refiner	A, H	65–90
Green liquor	Na_2CO_3 + Na_2S	Disk refiner	A, H	65–90
Nonsulfur	Na_2CO_3 + NaOH	Disk refiner	A, H	65–90
Chemical Processes				
Kraft (High yield)	Na_2S + Na_2OH	Disk refiner	A, H, S	55–65
Sulfite (High yield)	Acidic sulfite (Ca, Na, Mg)	Disk refiner	A, H	55–70
	Or Bisulfite (Na, Mg)			
Kraft (+AQ)	Na_2S + Na_2OH (+AQ)	Mild to none	A, H, S	45–55
Kraft (Polysulfide)	$(Na_2S + Na_2OH)_X$	None	A, H, S	45–60
Soda	NaOH	None	A, H	40–55
Soda-AQ	NaOH + AQ	Mild to none	A, H	45–55
Soda-oxygen	NaOH, O_2	Disk refiner	A, H	45–60
Acidic sulfite	Acidic sulfite (Ca, Na, Mg, NH_3)	Mild to none	A, S	45–55
Bisulfite	Bisulfite (Na, Mg, NH_3)	Mild to none	A, H, S	45–60
Neutral sulfite	Neutral sulfite	Mild to none	A, H, S	45–60
Magnefite	Mg-bisulfite	Mild to none	A, H, S	45–60
Muti-stage sulfite	Na_2SO_3 + $NaHSO_3/SO_2$	None	A, H, S	45–55
	or $NaHSO_3$ +SO_2/Na_2CO_3			
Alkaline sulfite	Na_2SO_3 + NaOH	None		
Dissolving Processes				
Acid sulfite	Acid sulfite (Ca, Na)	None	A, H, S	35–42
Prehydrolysis Kraft	Prehydrolysis + kraft	None	A, H, S	30–35

*: Source: Fengel and Wegener, 1984.

**: A: annual plants; H: hardwood; S: softwood.

Table 10. Pulping processes for annual plants

Pulping process	Chemical treatment	Mechanical treatment	Frequency
Chemical pulping			
Soda (+AQ)	NaOH (+AQ)	None	Commonly used
Kraft (+AQ)	Na_2S + Na_2OH (+AQ)	None	Commonly used
Sulfite	$NaHSO_3$ and/or SO_2/Na_2CO_3	None	Commonly used
Phosphate	Na_3PO_4	None	Potentially used
Milox	Formic acid	None	Potentially used
Impregnation-Depolymerization-Extraction (IDE)	NaOH, sodium carbonate, ethanol-water blend	None	Potentially used
Alcell	Ethanol-water blend	None	Potentially used
Processes other than chemical pulping			
Thermomechanical	Steam	None	Potentially used
Biopulping	White rot fungi	Disc refiner	Potentially used
	Ceriporiopsis subvermispora	Disc refiner	Potentially used
Alkaline peroxide mechanical pulping (APMP)	NaOH, H_2O_2	Disk refiner	Potentially used
Chemi-thermomechanical (CTMP)	Steam + $NaHSO_3$ + NaOH	Disc refiner	Potentially used
Cold caustic soda mechanical	NaOH	Disc refiner	Potentially used
IRSP	NaOH (+AQ) + Steam	None	Potentially used

2.3.2.1. Mechanical pulping

Mechanical pulps are obtained by disintegrating and physically separating the fibers. These pulps have a very intense color and are often used for newspapers or paperboards. Because of the large quantity of residue lignin in the pulps, the color of these pulps easily turn yellow, but this can be overcome by subsequent chemical bleaching. Softwood is the most common raw material of mechanical pulps, which are relatively white. Annual plants are the easiest materials to use with mechanical pulping because of their porous stalks. Mechanical pulping does not use chemicals to eliminate lignin and hemicellulose, so yield is often high (90-98%) (Table 9).

2.3.2.2. Chemical pulping

With chemical pulping, delignification is carried out with the help of acidic or alkaline reagents in reactors. The lignin and hemicellulose are partially eliminated so yields are between 40 and 60%. On the other hand, the fibers are whiter and better separated. Chemical pulping is divided into sulfite pulping and alkaline pulping depending on the pH and nature of the pulping reagents. Sulfite pulping is a stronger process because the separation of the cellulose is better and their pulps can be used to produce chemicals and papers of particularly good quality. The disadvantage of sulfite pulping is that it cannot use resinous wood, because at low pH the phenols of the resins and acids condense with the lignin to form an insoluble, color complex that stains the pulps. With alkaline pulping, on the other hand, these complexes are eliminated in the residual. Alkaline pulping—especially kraft pulping, which can use variable raw materials—is the dominant method.

Soda process

This is the oldest and simplest pulping process. The soda process is a common way to produce annual pulp. With this process, the cooking chemical is mainly sodium hydroxide. Soda process leaves more insoluble carbohydrates in the pulp and obtains a better yield than the kraft method (Patt et al., 1986). The strength and lignin content of pulps produced with the soda and Kraft processes are similar. Easily bleachable short fibers that are abundant in pentosan are produced. This process often uses easily pulped species such as cereal straws, flax, abaca etc. (Kokurek et al., 1989; Kulkarni, 1989a; Jiménez et al., 1993).

Holton (1977a) proposed a soda pulping process in which a catalyst, anthraquinone (AQ), is added. This catalyst has two fundamental effects: the alkaline delignification process is accelerated and the carbohydrates are stabilized. Soda-AQ pulping improves the yields under the same operation conditions as conventional soda pulping. The use of this catalyst (AQ) is only limited to 0.1% of the dry biomass.

Since annual plants are impregnated easily (Ye et al., 2003) and have a low reactive lignin content (Table 7), the amount of pulping chemicals needed for annual plants is lower than for woods. With soda pulping, 10–15 % NaOH, which depends on the raw material, is normally used at a pulping temperature of 160–170 °C (Patt et al., 1986). Yields range from 40 to 55 % and are influenced greatly by the species and quality of the raw material, especially the lignin content and the proportion of parenchyma cells (Han and Rowell, 1996). A high parenchyma content increases the formation of fines, which not only reduces the yield and increases alkali consumption but also reduces the dewatering properties and strength of the pulp (Patt et al., 1986; Han and Rowell, 1996).

Kraft process

Kraft pulping is the most important pulping method. At present, more than half of the worldwide production of pulps is manufactured using this method (Wenzl, 1970; Fengel and Wegener, 1984; Bryce, 1990). Yields vary between 40 and 60%. Kraft pulping requires shorter cooking times and is not very selective. The pulping chemicals used are mainly NaOH and Na_2S (Clayton et al., 1989; Bryce, 1990a). The raw material is treated with a highly alkaline solution of NaOH, which is known to cleave lignin but also eliminates some of the hemicellulose. The undesirable breakdown of hemicellulose is largely avoided by adding Na2S to the solution, which avoids a very high concentration of NaOH in the pulping liquor (McDougall et al., 1993). Kraft pulping usually operates in batch reactors with a temperature between 160 and 180ºC and a cooking time between 4 and 6 hours. Continuous kraft pulping operates at a temperature between 190 and 200ºC and a cooking time between 15 and 30 min (Kortelainen and Backlund, 1985). New kraft pulping technologies concentrate on reducing the high emissions of sulfurated compounds generated during pulping and of compounds that contain reduced sulfur (RS) produced at various stages of pulping (Fagerström, 1993).

Sulfite process

The main pulping chemicals are $NaHSO_3$ and/or Na_2SO_3 (Atack et al., 1980; Costantino et al., 1983). The reactors for this process can be continuous or batch and operate at temperatures between 125 and 180ºC depending on the final product (paper, cardboard, etc.). This process has a yield of between 40 and 60%. In the pulping process, sulphonates form and are hydrated and the swelling of fibers helps delignification. The strongly ionized sulphonic acids increase the acidity of the pulping medium, which results in condensation reactions between phenolic moieties in lignin. This forms insoluble resin-like polymers. These side reactions include degradation of the hemicelluloses and celluloses. However, these carbohydrates are less degraded, which causes a higher degree of polymerization and therefore a lower resistance of the pulps than in the kraft process. Sulphite pulps are easier to bleach and are used to produce paper with specific properties, such as toilet and tissue paper, which must be soft, absorbent, and strong (McDougall et al., 1993).

IRSP (Impregnation rapid steam pulping process) process

Montané et al. (1996) developed the IRSP process using wheat straw, which is also tested by other annual plants and woods such as pine, miscanthus, sugar cane, cardoon, and eucalyptus (Barba et al., 2002; Ye and Farriol, 2003). This process differs from steam explosion pulping in the nature of the impregnation, which generally uses concentrated NaOH solutions, moderate pressures, and short impregnation times of 1–2 hours. This process consists of two steps: (1) impregnation and (2) rapid steam pulping.

(1) Impregnation

The aim of impregnation is to obtain a uniform distribution of pulping chemicals in chips. Uniform distribution leads to more uniform pulp, better quality, fewer rejects, and shorter cooking times (Gustafsson, 1988; Gullichsen and Sundqvist, 1995). The reactive pulping chemicals are mass-transferred into the stalk voids by penetration (which is governed by the pressure gradient) and by diffusion (which is controlled by the concentration gradient of the penetrating chemicals) (Stone and Forderreuther, 1956).

NaOH and anthraquinone (AQ) are used as pulping chemicals under mild pressure. Chemicals penetrate and diffuse into the capillaries and stalk voids. The stalk fibers swell until maximum absorption is reached. Water, NaOH, AQ, and alkaline soluble chemicals transfer between the fiber and the bulk solution until an equilibrium stage is reached.

Delignification, the softening of fibers, and defibration occur during the swelling and penetration stages. Some lignin that reacts with NaOH degrades and dissolves in the alkaline solution. The initial white color of the alkaline solution becomes darker and blacker (Ye and Farriol, 2005).

(2) Rapid steam pulping

Explosion pulping was invented by Mason (1928). Vit and Kokta modified, improved, and developed the process to produce pulps that are suitable for papermaking (Vit and Kokta, 1986) using techniques such as the chemical impregnation of chips, short-duration saturated steam cooking and sudden pressure release (Vit and Kokta, 1986; Kokta and Vit, 1987; Kokta and Ahmed, 1998). Steam explosion pulping can be divided into two stages: rapid steam cooking and steam explosion.

In the rapid steam cooking stage, typical cooking time is several minutes and typical cooking temperature is above 180^0C. The short cooking time prevents side reactions and improves the selectivity and the yield of pulps. Water has a plasticizing action on the glass transition temperature of lignin and hemicellulose, and their softening temperature is reduced to about 100^0C. Steam cooking at temperatures above their glass transition temperature leads to additional permanent fiber softening because of internal structural changes (Kokta and Ahmed, 1998). Structure softening leads to defibration. Lignin reacts with residual NaOH that is absorbed in the fibrils and degraded. AQ protects the cellulose and hemicellulose and increases the yield of pulping during steam cooking at high temperature (Abott and Bolker, 1982; Blain, 1983). The more uniformly distributed NaOH and AQ are in the fibrils, the better is the quality of the pulps. Cellulose is degraded and some of it is converted to polysaccharides. Hemicellulose is also degraded and some of it is converted to polysaccharides. Degraded lignin and low-molecular-weight polysaccharides dissolve in alkaline aqueous solutions. These degraded substances diffuse into the bulk cooking liquid. The places they occupied are therefore vacant and gradually develop into capillaries and voids. During the cooking process, more and more voids appear. The increasing numbers of voids helps and improves the effect of the subsequent steam explosion pulping.

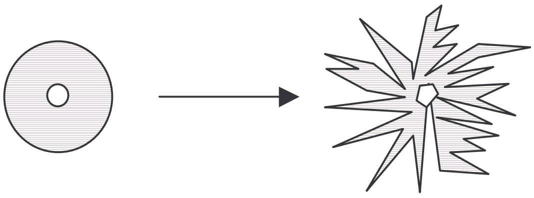

Figure 12. The steam explosion effect of a fibril

During steam cooking, interior capillaries and fibril voids are gradually filled with high-pressure liquid. When the cooking pressure is suddenly released, the high-pressure liquid evaporates, which subjects the fibers to high impact forces. The fibers are lacerated (see Figure 12). The mechanical explosion tears and breaks the fibers from the interior capillaries and voids and produces smaller fibers, fibrils, and micro-fibrils. The surface areas of pulps increase significantly. This is the defibration, defibrillation, and laceration of the steam explosion process. The chemical pretreatment during impregnation swells and softens the fibers, and also probably dissolves some lignin or has some disintegration and defibration effects. Physical pretreatment of the chipped stalks (i. e. compression and decompression during impregnation under 15 bar pressure and further compression before steam cooking over 180^{0}C) considerably deforms and partially separates the fibers (Vit and Kokta, 1986; Kokta and Vit, 1987; Kokta and Ahmed, 1998). Steam cooking leads to softening, which is probably the result of defibration, and defibrillation in the interior fiber structure (Kokta and Vit, 1987). Explosion promotes defibration and probably some internal fibrillation. As a result, steam explosion pulping produces pulps that have higher yields, lower lignin contents, higher porosities, higher specific surface areas, and higher hydrophilicity than traditional pulping (Kokta and Ahmed, 1998). These pulps therefore have higher accessibilities and reactivities, which help pulp dissolution and cellulose derivation.

Pulping with organic solvents

Organic solvents combined with sodium hydroxide, sodium carbonate or other pulping chemicals have been studied as innovative pulping processes (Kinstrey, 1993; McDonough et al., 1993; Jiménez and Maestre, 1997). Both annual plants and woods have been studied using these processes.

ASAM (Alkaline sulfite-anthraquinone-methanol) process

Patt and Kordsachia developed this pulping process using methanol, sodium hydroxide, sodium carbonate, sodium sulfite, and anthquinane as pulping chemicals (Black, 1991; Patt et al., 1986). These pulps have similar resistance properties to the kraft pulps and similar bleaching properties to the sulfite pulps. Softwoods and hardwoods as well as annual plants have been tested with this process. This process can produce pulps of satisfactory properties that can be easily bleached by ECF or TCF bleaching sequences.

Organocell process

Organocell Thyssen GmbH developed this pulping process (Young, 1992) in which sodium hydroxide, methanol and anthquinane are used as pulping chemicals (Schroeter, 1991).

Alcell process

Repap Enterprises, Inc. developed this process using water and ethanol as cooking media at 180-200ºC (Alcell, 1991; Pye et al., 1991; Williamson, 1987). Based on a pilot scale, pulp yields and quality are comparable to those of conventional pulps (Winner et al., 1991).

Acetocell process

With this process, acetic acid, chloride acid, and sulfuric acid are used as the pulping chemicals. This process has been tested with annual plants, softwoods and hardwoods (Benar and Schuchardt, 1994; Vázquez et al., 1995; Jiménez and Maestre, 1997).

Milox process

The MILOX pulping and bleaching method is based on formic acid and hydrogen peroxide. Silica remains in the pulp after cooking but this can be dissolved in the alkaline bleaching process (Barba, 2002).

The IDE (Impregnation – Depolymerization – Extraction) process

With this process, the chipped stalk is first impregnated with a mixture of sodium hydroxide and sodium carbonate (Backman et al., 1994). In the depolymerization stage, the impregnated stalks are cooked in ethanol-water solution at a temperature of 140–190°C. In the extraction stage, residual lignin is extracted from the pulp with an aqueous ethanol solution. In this process, the silica problem remains partly unsolved, which is the main shortcoming of annual plants that are used as the raw materials of pulping and bleaching (Hultholm et al., 1995).

Pulping processes for dissolving pulps

In the production of dissolving pulps, the pre-hydrolyzed delignification of fibers can be carried out by the above pulping processes. However, the conditions of the pulps should be less severe, otherwise the pulps would have a very low viscosity and bad physical properties for the production of cellulose derivatives. The characteristic parameters of the processes for producing dissolving pulp (degree of polymerization, index of crystallinity, etc.) are intimately related to pulping severity. The hemicellulose is hydrolyzed or depolymerized, and separated in a form of soluble monosaccharide or oligosaccharide in aqueous solution. The lignin and hemicellulose contents in the resultant dissolving pulps are therefore very low. The cellulose produced by thermomechanical processing generally has a higher degree of crystallinity and a substantially lower degree of polymerization than cellulose produced by other pulping processes. The morphological structure of the fibers is strongly modified by the chemical pulping, so defibrillation is high. The cellulose has short fibers and a considerable amount of broken fibers. These characteristics are not suitable for producing paper but the pulps can be used to manufacture regenerated cellulose, cellulose derivatives, and microcrystalline cellulose of low molecular weights.

2.4. Bleaching

Pulp bleaching is carried out in a sequence of several stages to eliminate as much residual lignin as possible. Usually lignins are physically dissolved in alkaline solution or chemically modified to form soluble chemicals in aqueous/alkaline solutions (Singh, 1979; Garcia et al., 1984; Kokurek et al., 1989; Reeve, 1989). During bleaching, the lignins are oxidized, degraded, dissolved, and therefore decolored. Not all the colorful materials can be eliminated in a single process, however, so a multiple bleaching procedure is often used. This process often uses two types of reagents—oxidants and alkali—though reductants are sometimes used (Szilard, 1973). The oxidants are used to degrade and whiten the lignins. The alkali is used to dissolve the lignin. The alkali extraction can also be used to eliminate hemicellulose if the objective is to obtain dissolving pulps (Hinck et al., 1985). The following bleaching stages are often used in the contemporary bleaching industry (Szilard, 1973; Patt et al., 1986).

Chlorination (C)

Chlorine is a common, effective, selective bleaching agent that reacts quickly with lignin to form water-soluble degraded chemicals, which can be extracted with alkaline solution (Szilard, 1973). Chlorination is carried out at about 30^0C and usually lasts for 30 min for sulfite pulp and up to 60 min for kraft pulp at a consistency of about 3 % (Szilard, 1973; Patt et al., 1986). Shortly after this chlorination bleaching, the next bleaching process is alkaline extraction.

Alkaline extraction (E)

Alkali solution can dissolve some degraded lignins, degraded hemicelluloses and some depolymerized celluloses of low molecular weights (Szilard, 1973). Alkaline extraction is often carried out using 1–1.5 % NaOH (based on o.d. pulp) for sulfite pulps and 3 % for kraft pulps, which often lasts for 60–90 min at 40–60 °C at a consistency of about 10 % (Szilard, 1973; Patt et al., 1986). If dissolving pulps of extremely high α-cellulose contents are needed, the extraction temperature may be as high as 90 °C and the alkali charge as high as 5 % NaOH based on o.d. pulp (Szilard, 1973).

Hypochlorite bleaching (H)

The oxidation reagents attack the free phenolic hydroxyl groups or the phenolic ethers of the phenylpropane side chain of lignins (Szilard, 1973). Usually, 1–2 % hypochlorite based on o.d. pulp is used at 30–50 °C at a consistency of 10 % and the bleaching lasts for 2–4 h (Szilard, 1973; Patt et al., 1986).

Chlorine dioxide bleaching (D)

Chlorine dioxide is an extremely effective and selective bleaching reagent (Szilard, 1973). The chlorine dioxide attacks phenolic OH groups of lignins (Szilard, 1973). Phenoxy radicals formed in this way undergo further reactions either to provide quinoid structures or to form muconic acid derivatives after a ring cleavage. Chlorine bleaching uses 0.5 and 1.5 % active chlorine based on o.d. pulp, which is carried out at 70–80 °C for 3 – 4 h at a consistency of 10–12 % (Patt et al., 1986).

Oxygen bleaching (O)

The bleaching agent is gaseous oxygen. The process must be carried out under mild pressure for a sufficient amount of oxygen to be available in the bleaching liquor (Patt et al., 1986). As a biradical, oxygen can remove an electron from the phenolate ions, which present in the alkaline medium. The formed phenoxy radical undergoes further degradation reactions. Hydroperoxides are produced, which are further degraded by intramolecular nucleophilic attack of the peroxide anions. The oxygen bleaching, in which 2 – 4% alkali and 1 – 2.5% oxygen are used (Patt et al., 1986), lasts 30 – 90 min.

Ozone bleaching (Z)

The most important reaction of ozone with lignin is the cleavage of the bonds between the lignin units (Patt et al., 1986). Ozone can attack both the aryl and the alkyl moieties (Patt et al., 1986). The attack on the aromatic rings leads to ring cleavage. Double bonds in the aliphatic side chain, where carbonyl and peroxide structures are formed, are also attacked.

Peroxide bleaching (P)

The bleaching of mechanical pulp destroys the chromophoric groups by cleaving conjugated double bonds (Szilard, 1973). At 70–80 °C, the highly nucleophilic perhydroxyl ion formed can further degrade quinoid lignin structures, which are produced by the electrophilic bleaching chemicals. The peroxide bleaching uses 1–2 % based on o. d. pulp at a consistency of 10 % at 70–80 °C (Szilard, 1973; Patt et al., 1986).

Traditionally, the bleaching reagents are chosen for their economy and selectivities as well as their capacity for bleaching efficiency and quality. Currently, due to the strict environmental restrictions on the emission of organic chlorides and dioxins in effluents, the bleaching sequences increasingly use Elementary Chlorine Free (ECF) or Totally Chlorine Free (TCF) processes (Kinstrey, 1993). TCF bleaching is the current trend for contemporary delignification. TCF bleaching produces no organochlorines, which are hazardous substances such as dioxin, an endocrine disrupter, and human carcinogen (Szilard, 1973).

2.5. Cellulose derivatives

Cellulose cannot dissolve in water. Introducing hydrophilic groups along the chain of cellulose cleaves hydrogen bonds and renders its derivatives soluble in conventional solvents, widening its applications to, for example, functional cellulose ethers and esters (Greminger, 1979; Fengel and Wegener, 1984; Coffey and Bell, 1995; Zhang, 2001).

Commercial cellulose derivatives are either ethers or esters that are soluble in water or organic solvents. The three free hydroxyl groups in the AGUs react with various functional substitution groups. The resultant substituents therefore disturb the inter- and intra-molecular hydrogen bonds in cellulose, reduce the hydrophilic character of the numerous hydroxyl groups, and increase the hydrophobicity. Introducing ester and ether groups separates the cellulose chains so completely that the fiber structure is either altered or destroyed. The solubility of a cellulose derivative in a solvent or in water depends on the type of substituents, the degree of substitution and the molecular weight.

These cellulose derivatives are grouped according to the processes and chemical substituents. The most important commercial cellulose derivatives are shown in Figure 13 (Nikitin, 1962; Greminger, 1979; Hinck et al., 1985; McGinnins et al., 1990; Baehr et al., 1991).

Cellulose derivatives are usually produced from cotton or wood-dissolving pulps, which are pulped by a pre-hydrolysis pulping process and bleached to as low a lignin content as possible. These pulps are therefore cellulose of high purity with trace lignin and hemicellulose. Some authors have tried to synthesize cellulose derivatives directly from plant chips. Due to the lack of reactions between derivation reagents and fiber components (cellulose, lignin, hemicellulose, extractives and inorganic materials), this successful investigation or approach is only carried out in laboratory scale tests.

Cellulose derivatives have diverse physicochemical properties because of the types of substituents, degrees of substitution, molecular weights, and degrees of polymerization. They are mainly used, therefore, as additives of fine/special chemicals, such as cement additives, cosmetic additives, pharmaceutical components, diet additives, textile-treatment additives, painting additives, package materials and membrane materials, etc. (Balser, 1986; Brandt, 1986).

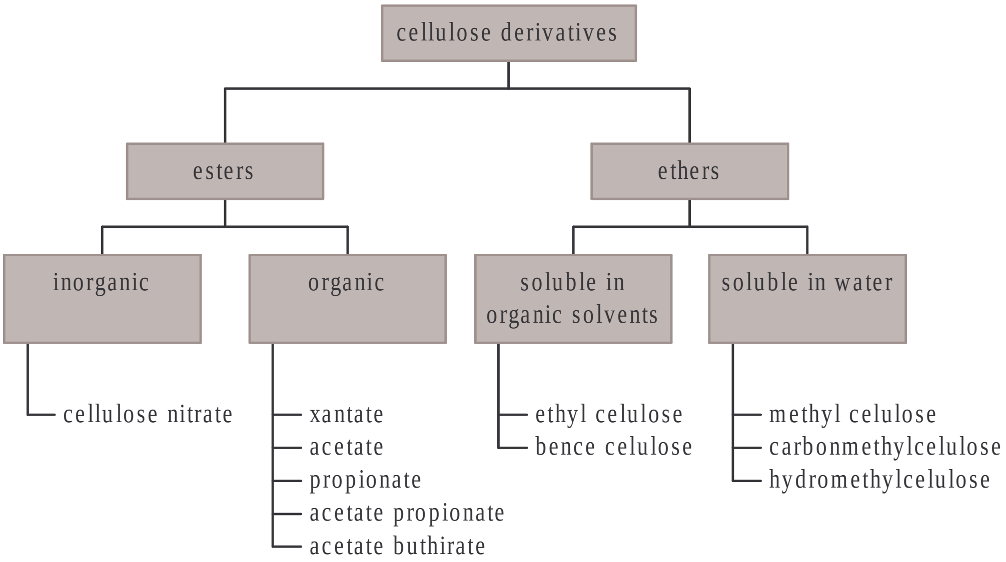

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Figure 13. Important cellulose derivatives

2.5.1. Cellulose esters

Cellulose esters are synthesized from inorganic acids as well as organic acids or their anhydrides. Cellulose may be considered as a trivalent polymeric alcohol with three free hydroxyl groups, which are polar and can be substituted by nucleophilic groups in strongly acid solutions. Esterification is in equilibrium with the reverse reaction (Balser et al., 1986).

Cellulose is a semi-crystalline solid in which crystalline cellulose (about 67%) and amorphous cellulose (about 33%) form the elementary fibril. The crystal interior is not freely accessible to the reaction reagents. The strong hydrogen bonds and weak van de Wall’s forces cause the molecular arrangement of cellulose and microstructure in the cellulose fibril, which both depend on the origin and previous physicochemical treatments. Accessibility to the reaction reagents and reactivity of the alcohol groups also depend on the nature of the cellulose structure.

Since cellulose is insoluble in all common solvents, cellulose esterification is usually carried out in heterogeneous slurries. This kind of reaction is usually a typical topochemical reaction. As the reaction proceeds, new reactive centers are created so that, finally, almost all fibrils of the cellulose fibers are reacted. Some yielded soluble derivatives are even further reacted in a homogeneous phase. The following two reaction types can occur during the esterification of cellulose (Balser et al., 1986).

1. An intermicellar reaction (Balser et al., 1986). The esterification chemicals initially penetrate and diffuse into the amorphous regions between the crystalline cellulose micelles. This penetration and diffusion then continue from the surface to the inner parts of the micelles, which are attacked and gradually disrupted by these reagents. The reaction of cellulose and acids is faster than the penetration and diffusion. The total reaction is therefore determined by diffusion.

2. An intramicellar or permutoid reaction (Balser et al., 1986). The reagents penetrate and diffuse into all parts, including the crystalline micelles so that all cellulose molecules react almost simultaneously. The reaction speed is determined by the esterification equilibrium.

Both reactions may occur and finally merge, depending on the reaction conditions—especially the reaction solvents, the nature of the cellulose, the mole ratio of reagents, and the temperature (Balser et al., 1986).

The esterification reactions are not carried out as stoichiometric reactions (Balser et al., 1986). The average degree of substitution of cellulose esters does not often reach the maximum (3). The degree of cellulose esters is often below three. The primary hydroxyl group on the C-6 atom is more reactive than the neighboring hydroxyl groups on the C-2 and C-3 atoms of the anhydroglucose unit, which are less reactive because of steric hindrance (Balser et al., 1986).

Over 100 types of cellulose esters are available but the most important ones are cellulose nitrate and cellulose acetate. The nitrate esters are produced by reacting the cellulose with a mixture of nitric acid, sulfuric acid and water (Balser et al., 1986). The highly nitrated cellulose with DS ranging from 2.4 to 2.8 is used to produce explosives and flammable solids. The less nitrated celluloses are used to produce tapes of movies, adhesive, shellacs and plastics. The applications of acetate cellulose depend on its DS. When the DS is less than 2.4, it is used to produce fibers or tapes of photographic movies. When the DS is above 1.4, it has better mechanical properties.

2.5.2. Cellulose ethers

Cellulose ethers are important cellulose derivatives. They can be dissolved in water or in organic solvents. Cellulose ethers have various substituents, degrees of substitution, degrees of polymerization and even various mixed substituents, which make them suitable for a wide range of applications in various industries, such as the food industry, the recovery of oils, paper, cosmetics, pharmaceutics, adhesive, agriculture, ceramics, textiles and construction (Brandt, 1986). The total production of cellulose ethers reached 387,000 metric tons in 1988 (Dönges, 1990).

Cellulose is mercerized with aqueous alkaline solution to yield swollen alkali cellulose. The alkali cellulose is then etherified with the chemicals under alkaline conditions. Sodium hydroxide is often used as the alkali, though other alkalis have different influences on both mercerization and etherification (Krässig, 1993). To synthesize mixed ethers, the various reagents may be reacted with cellulose simultaneously or in various stages (Brandt, 1986). There are two important types of etherification depending on the consumption of alkali (Brandt, 1986).

1. The Williamson etherification (Brandt, 1986). An organic halide is used as the etherification reagent to react with the alkali cellulose. Alkali is consumed stochastically. At the purification stage, the residual alkali in crude methylcelluloses must be washed out as salts.

2. The Michael addition (Brandt, 1986). The alkali functions as a catalyst during the addition of epoxides to the hydroxyl groups. No alkali is consumed although sufficient alkali must be retained during the etherification process. The alkali in the crude products must be neutralized before the purification stage.

The etherification can be carried out in heterogeneous or homogeneous systems as continuous or batch reactions. The cellulose ethers in heterogeneous system are produced by the following three steps: mercerization, etherification and separation or purification.

Mercerization

In modern mercerization processes, 30–70 % NaOH solution is sprayed onto dry cellulose powder in fast-turning, dry-mixing aggregates (Brandt, 1986). The cellulose powder can also be impregnated with an inert organic solvent, which is used to produce carboxymethyl cellulose (CMC) (Brandt, 1986). The cellulose can be mercerized in an organic solvent in normal stirred vessels, which use powder NaOH after the slurry of cellulose is formed (Brandt, 1986).

The alkali cellulose for subsequent etherification must contain at least 0.8 mol of NaOH per mole of anhydroglucose, which is a basic requirement to produce uniformly substituted ethers (Brandt, 1986). Cellulose ethers of lower viscosities are usually adjusted in the alkalization step, which is referred to as the ageing process (Brandt, 1986). In the ageing process, carefully designed conditions must be adjusted according to the product's final application. The optimum parameters often control ageing time, temperature, NaOH concentration and the presence of catalytic amounts of iron, cobalt, or manganese salts, which catalyze the oxidative depolymerization (Brandt, 1986).

Etherification

Cellulose ethers are preferably produced in slurry systems (Donges, 1990). Most reactions are carried out in organic systems in order to produce a final slurry in which solid ethers can easily be recovered. Another reason for this is that etherification is an exothermic reaction. In a slurry, the heating and cooling can be easily controlled. Organic solvents are selected in order to produce the most uniform alkali cellulose and be unreactive towards the reagents and products (Brandt, 1986). Some unreactive surfactants and amines have been added into the organic systems to improve penetration and swelling, respectively (Brandt, 1986).

Separation and purification

Any sodium hydroxide that is not consumed during the etherification process must be neutralized shortly after the end of the process. Crude cellulose ethers that are not soluble in hot water are washed with water at 80-90^{0}C. Crude cellulose ethers that are soluble in hot water are purified with a mixture of solvent and water (Donges, 1990). To improve the appearance, solubility and homogeneity of cellulose ethers, the following final treatments are often carried out: the addition of additives, crosslinking to adjust solubility, drying, grinding, and sieving operation (Donges, 1990).

2.6. Methylcellulose

Methylcellulose is an important cellulose ether. Alkali cellulose reacts with chloromethane, iodomethane, or dimethyl sulfate to form methylcellulose. The molecular structure is shown in Figure 14. The hydroxyl groups of cellulose are partially etherified. Methylcellulose is a white or slightly off white, fibrous or granular powder. The properties of methylcelluloses are influenced by their molecular properties i.e. their degrees of substitution (DS), molecular weights, molecular weight distribution, degrees of polymerization (DP) and distribution of methoxyl groups along the glucose unit and polymer chain. These properties strongly depend on the methylation conditions and properties of cellulose, which, in turn, depend on the bleaching conditions, pulping parameters, plant species, the time the plant is harvested and even parts of the plant.

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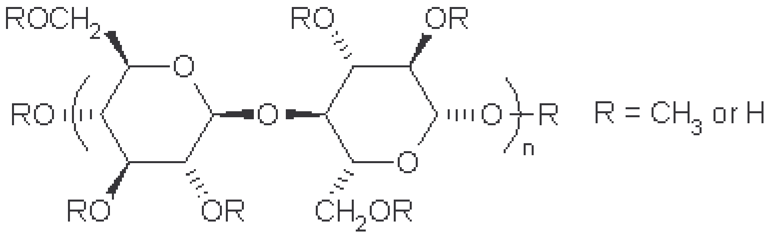

Figure 14. Chemical structure of methylcellulose

There are two types of commercial methylcelluloses depending on its solubility（Brandt, 1986）: (1) water-soluble methylcelluloses with a degree of substitution ranging from 1.4 to 2.0, which is produced and used widely, and (2) alkali-soluble methylcelluloses with a lower degree of substitution ranging from 0.25 to 1.0, which can be dissolved in 2–8 % aqueous NaOH solution. Methylcellulose solutions often contain insoluble particles due to non-uniform mercerization and subsequent partially uncompleted methylation. The insoluble particles in methylcellulose solutions can be removed by special alkalization techniques using NaOH-copper (II) complexes or benzyltrimethyl ammonium hydroxide as alkalizing agents (Krässig, 1993).

The industrial production of methylcellulose began in 1925 with the process of

Ernst and Sponsel, who used alkali cellulose to react with gaseous chloromethane (Ernst and Sponsel, 1925). Methylcelluloses are now produced in many counties. The total world production of methylcelluloses was nearly 70,000 tons in 1988 (Dönges, 1990). About 47% of this annual production is used in building materials, 21% in paints, 14% in wallpaper paste, 5% in cosmetics and pharmaceutical, 5% in polymerization, 4% in detergents and 4% in other minor applications (Dönges, 1990).

2.6.1. Viscosity

Viscosity is the most important property for the applications of methylcelluloses. Viscosity depends strongly on the concentration of the solution, the temperature, the addition of other chemicals and the most important features of methylcellulose, i. e. the degree of substitution, molecular weight, distribution of methoxyl group on the glucose unit, and distribution of methoxyl group on the cellulose chain, etc.

According to the Staudinger-Mark-Houwink equation, the relationship between the intrinsic viscosity (η) and the molecular mass (Mn) can be expressed as (Dönges, 1990):

°

$$[\eta] = K \times M_n^{\;a}$$

where *K* and *a* are polymer-specific constants.

° For methylcellulose, this equation can be expressed as (Dönges, 1990):

$$[\eta] = 2.8 \times 10^{-3} M_n^{0.63}$$

The viscosities of methylcelluloses are stable within the 2–12 pH range. When the temperature increases before the gelation point, the viscosity decreases (Brandt, 1986). The interaction of the dissolved methylcellulose molecules is reduced by mechanical stress, so the viscosity drops (Brandt, 1986). Osmometry or light-scattering methods are preferred for determining the average molecular mass and degree of polymerization (Table 11) (Brandt, 1986).

Table 11. Viscosities and molecular masses of methylcelluloses*

Apparent viscosity at 2 % and 20 °C (mPas)	10	40	100	400	4000	8000	19000
Intrinsic viscosity (ml/g)	140	205	265	390	750	930	1200
Average molecular mass**	13000	20000	26000	41000	86000	110000	140000
Average degree of polymerization**	70	110	140	220	460	580	750

*: Source: Brandt, 1986.

**: Osmometry method.

2.6.2. Gelation

Methylcellulose solution has a special gelation phenomenon that is caused by heating to form a gel and cooling to form a clear solution reversibly (Haque, 1993; Hirrien, 1996). Pure methylcellulose solutions gel at about 50-65^{0}C, which depends on the structure of methylcellulose (Brandt, 1986; Haque, 1993).

Typical methylcelluloses of DS 1.8 form a gel at 54-56 °C (Hirrien, 1996). Gelation temperatures of water-soluble methylcelluloses drop as the degree of substitution increases (Brandt, 1986; Haque, 1993). Gelation temperatures of a given degree of substitution decrease little as the viscosity of the solution increases (Brandt, 1986). Added electrolytes lower gelation temperatures, which depend on the types and quantities of salts added (Levy and Schwarz, 1958; Xu et al., 2004 a and b). Some salts even prevent the dissolution of methylcelluloses at ambient temperature (Levy and Schwarz, 1958). Both heat and electrolytes destroy hydrated structures by breaking hydrogen bonds between water and the polymer (Levy and Schwarz, 1958; Brandt, 1986; Haque, 1993). When polar water-miscible organic solvents such as alcohols or glycols are added, methylcellulose solutions stabilize (Kundu et al., 2003). Methylcellulose and these polar additives therefore form strong hydrogen bonds that increase gelation temperatures and lead to more stable soluble complexes in the solution (Brandt, 1986; Kundu et al., 2003). Methylcelluloses are incompatible with some additives, such as tannin, because they form insoluble complexes even at low additive concentration (Levy and Schwarz, 1958; Brandt, 1986).

2.6.3. Solubility

Methylcellulose becomes soluble in ethanol when the DS is over 2.1 (Croon and Manley, 1963). If the DS is over 2.4, it is also soluble in solvents such as acetone or ethyl acetate (Croon and Manley, 1963). When the DS is over 2.7, the methylcellulose is even soluble in some hydrocarbons (benzene, toluene) (Croon and Manley, 1963). Methylcelluloses are soluble in different solvents depending on the DS (see Table 12). This table 12 is only a rough guide because other factors, such as molecular weight, manufacturing processes, distribution of substituents and treatments, also influence solubility. Because of the solubility in different solvents and the special gelation, methylcelluloses can be purified and separated, and their properties can even be measured in some common solvents using modern technologies.

Table 12. The solubility of methylcelluloses according to DS

DS	0.1 – 1.0	1.4 – 2.0	2.4 – 2.8
Water	Swelling	Soluble	Insoluble
4% NaOH solution	Soluble	Swelling	Insoluble
Acetone	Insoluble	Insoluble	Insoluble
Methanol	Insoluble	Insoluble	Insoluble
THF	Insoluble	Insoluble	Soluble
Chloroform	Insoluble	Insoluble	Soluble
DMSO	Partially soluble	Soluble	Partially soluble
DMAc	Partially soluble	Soluble	Partially soluble

2.6.4. Synthesis

In 1905 Suida was the first to synthesize methylcellulose with dimethyl sulfate (Suida, 1905). Several years later, patents in which chloromethane was used as a methylation agent were published independently (Lilienfeld, 1912; Leuchs, 1912; Dreyfus, 1912). Cellulose is homogeneously methylated in triethylbenzylammonium hydroxide (Bock, 1937), trimethylbenzylammonium hydroxide (Stuchlík, 1956), LiCl/N,N-dimethylacetamide (McCormick, 1979), SO_2-diethylamine-methyl sulphoxide (Isogai, 1985) and LiCl/dimethyl sulfoxide (Petrus, 1995). The activation of cellulose is the most important step in homogeneous methylation. Sodium hydroxide powder (Isogai, 1985) and dimsyl sodium (Petrus, 1995) are used as activation agents in. In heterogeneous methylation, caustic alkaline solutions are used to mercerize cellulose and form alkali cellulose; methylcelluloses are synthesized in organic slurry with toluene (Denham and Woodhouse, 1914; Steele, 1949) or isopropanol (Tapia, 1996). Timell and Purves found that the heterogeneous methylation is intermicellar with dimethyl sulfate, while the uniform substituent distribution of commercial methylcelluloses indicates that it is intramicellar with chloromethane (Timell and Purves, 1951). Philipp et al. synthesized methylcelluloses with chloromethane to study methylation on the laboratory scale (Philipp, 1979). Taipa C. synthesized methylcelluloses from commercial pulps with dimethyl sulfate and iodomethane in 2-propanol slurry at 30^0C (Tapia, 1996).

Ye and Farriol developed a facile novel methylation method using iodomethane to prepare methylcelluloses from both wood and annual plants (Ye and Farriol, 2005a). This methylation procedure used IRSP pulping and TCF bleaching sequences to obtain bleached pulps that were mercerized in 40% NaOH solutions and reacted with iodomethane in isopropanol slurry at 60^0C for 22 hours. This method is very suitable for the synthesis of methylcellulose in laboratories.

Industrial Production

Methylcellulose is now produced in industry by methylating alkali cellulose with chloromethane under high pressure. Between 35 and 60 % aqueous NaOH is used in the mercerization. The molar ratio of NaOH to anhydroglucose unit must be 3:4 to obtain water-soluble ethers with DS between 1.4 and 2.0. The viscosity of alkali cellulose is adjusted by ageing with or without ageing catalysis. Usually an excess of chloromethane, depending on the amount of alkali, is used. Chloromethane reacts with water, which produces the byproducts methanol and dimethyl ether. The crude methylcelluloses produced require acid neutralization to remove residual alkali.

Methylcellulose can be produce under mild pressure in a batch reactor with gaseous chloromethane (Brandt, 1986). Alkali celluloses methylate with the chloromethane at 60–100 °C for several hours (Brandt, 1986). During methylation, some reagents evaporate with volatile byproducts. These are removed and condensed. The chloromethane is then recycled and replenished with fresh reagent to keep the concentration of gaseous chloromethane constant (Brandt, 1986).

Another methylation method is to produce methylcellulose under higher pressure in a continuous reactor with liquid chloromethane. Typically, methylation is carried out in a reaction time of less than 1 h with or without an inert organic liquid (Brandt, 1986). This process consists of slurrying the alkali cellulose under pressure in excessive chloromethane. The slurry is then pumped through a partially heated reaction tube. Volatile byproducts and excessive chloromethane are evaporated. Filtration is often used to separate the crude methylcellulose.

Techniques for optimizing methylation have been investigated e.g. the choice of slurry solvents, the gradual addition of reagents and temperature-programmed reaction steps etc. (Brandt, 1986). Sodium chloride and other nonvolatile byproducts are removed by washing with hot water above the gelation temperature of the methylcellulose. The product is then dried and ground in conventional equipment.

2.6.5. Applications

The applications of methylcelluloses depend on their chemical and physical properties (Krassig, 1993). The properties of methylcelluloses mainly depend on their molecular weights and degrees of substitution (Croon & Manley, 1963), the distribution of methoxyl groups along the glucose unit and the cellulose chain (Brandt, 1986), and the distribution of molecular weights.

Methylcelluloses function as surfactants in aqueous systems by reducing surface tension and supporting emulsification of two-phase layers. The amphiphilic character is due to the presence of both hydrophilic OH and hydrophobic OCH_3 groups in a single methylcellulose molecule. Their viscosity is excellent during long-term storage due to resistance against fungi and bacteria attack. Methylcelluloses improve the properties of cement-based products and ceramic extrusions thanks to their lubricant and water-retention properties. Methylcelluloses function as thickening additives and improve adhesion degree of formulations. Methylcelluloses form clear, tough, flexible films that have excellent barrier properties to oils and greases. Methylcelluloses enhance the stability of suspension throughout the solution due to the formation of hydrogen bonds. They are soluble in some binary organic and organic-water solvent systems because they have hydrophobic groups in their molecules. Methylcelluloses dissolve more easily in cold water than in hot water. They can reduce water-loss when its formulations are applied to water-absorbing surfaces. They have excellent water-retention properties, being used in cement and gypsum formulations and in water-based paints and wallpaper adhesives, where the cohesiveness of the products is also important. Water retention increases as the number of hydrophilic groups and the viscosity increase. Typical applications for methylcelluloses are gels and fine or special chemicals in the pharmaceutical industry, foods, construction, paints, ceramics, detergent, agriculture, polymerization, adhesives, cosmetics, and tobacco (Brandt, 1986).

Methylcellulose gels

Methylcellulose gel can be controlled by modern technologies. The gelation temperatures can be adjusted by the degree of substitution, molecular weight and addition of additives (salts, alcohols etc.) (Levy and Schwarz, 1958; Kundu et al., 2003; Xu et al., 2004 a and b). Methylcellulose gel is used as a contrast agent for ultrasound examination of the cervix (O'Brien et al., 2003).

Foods

Methylcelluloses are approved as internal food additives in the United States, the European Community and many other countries. They are used as binders, thickeners, form stabilizers, suspending agents and bulk materials in sauces, ice cream, gravies, baked goods, dietetic foods and salad dressing, etc.

Pharmaceutical industry

Methylcellulose is an effective medicine for eye or other illnesses (Knight, 1952). Methylcelluloses of low viscosity are used for tablet coatings (Wan, 1986). Methylcelluloses are also used as drug carriers, tablet disintegrators and stabilizing agents for suspensions and emulsions (Wan, 1986). They are used as bulk laxatives, which are dispersed readily in sufficient amounts of water and are not metabolized. The suspending property of methylcelluloses is used for the better dispersion of barium sulfate in X-ray diagnosis.

Construction industry

Methylcelluloses are useful additives in construction materials because of their binding, suspension-stabilizing, and water-retaining properties (Donges, 1990). They are used in most cement- or gypsum-based formulations, such as masonry mortars, grouts, cement coatings, plasters, jointing compounds and emulsion putties (Donges, 1990). Methylcelluloses improve the dispersion of sand or cement (Brandt, 1986). They further intensify adhesiveness, which is important for plasters, tile cement and putties. Methylcelluloses are often used in combination with gluconates in mortars as valuable set-retarding additives. In wallpaper glues, they are used as thickeners and adhesives, usually combined with polyvinyl acetate, CMC and/or starch derivatives. Methylcelluloses of medium and high viscosity are preferred in construction materials and wallpaper glues (Donges, 1990).

Paints

Methylcelluloses are used in latex and distemper paints (Donges, 1990). They act as thickeners and as suspension aids for pigment particles (Donges, 1990). Directly adding the methylcellulose to the pigment grind is possible by choosing glyoxal-crosslinked products with retarded dissolution. Organic-soluble methylcelluloses are used in solvent-based paint removers to prevent evaporation of the solvent, e.g. as a dichloromethane-alcohol mixture. Water-soluble methylcelluloses are used in aqueous coatings (Brandt, 1986).

Ceramics

Methylcelluloses can be used in the production of ceramics as green strength binders with good burnout properties (Brandt, 1986). Methylcelluloses of pure grades are preferred because they do not cause ash residues.

Detergents

Methylcelluloses have become interesting for use in detergent formulations (Donges, 1990). They exhibit some soil-suspension action in fabrics based on synthetic fibers. Methylcelluloses have both hydrophilicity and hydrophobicity because of their hydroxyl and methoxyl groups on the molecular chains.

Agriculture

Methylcelluloses function as suspending agents for solid pesticides in water-based sprays (Donges, 1990). They are used in slurries for seed treatment to increase the seed coverage and reduce exposure hazards caused by dusting of the protectant. Low-viscosity methylcelluloses are applied in amounts of 25–050 %, depending on the mass of the dry protectant (Brandt, 1986). Medium-viscosity methylcelluloses are also added to agricultural dusts at a level of 6–12 % of the dust to obtain better adhesion when the dust is wet by rain or dew (Brandt, 1986). Wettable powders are better dispersed when 0.5–2 % of low-viscosity methylcelluloses is added (Brandt, 1986).

Polymerization

Methylcelluloses are used as suspension stabilizers and protective colloids in vinyl chloride polymerization for uniform particle distribution (Donges, 1990). Clearly soluble and highly purified types of low viscosity are required for this purpose. They are used in both emulsion and suspension techniques for the polymerization of styrene and vinyl acetate, as well as for copolymerization processes (Brandt, 1986).

Adhesives

Methylcelluloses are used as additives in numerous adhesive formulations (Donges, 1990). They are especially convenient in the leather industry (Brandt, 1986). Hides are pasted onto large frames of different materials by adhesive formulations containing methylcelluloses. The hides are then passed through a heating zone to dry. This causes the methylcelluloses to gel, which results in excellent adhesive bonds and fewer drop-offs during subsequent tanning (Brandt, 1986).

Cosmetics

Methylcelluloses function as thickeners, stabilizers, suspending agents and film formers in creams, lotions and shampoos (Donges, 1990). As methylcellulose provides a barrier against oil-soluble materials, it is used in protective creams against irritants ranging from tear gas to paint (Brandt, 1986).

Tobaccos

Methylcelluloses are used in the foil and flake of tobacco industry as film formers and binders (Brandt, 1986).

3. Experimental

3.1. Materials

3.1.1. Plant materials

Experiments were carried out using a homogeneous batch of each plant: dried miscanthus stalks, two years old eucalyptus chips, dried cardoon stalks harvested in summer, and spring cardoon stalks with leaves and capitula. These plants were all harvested in Spain. Barks of the eucalyptus chips were removed by hand. For a composition analysis, sawdust with a maximum size of 4-mm-mesh was used in order to ensure a kinetic and non-diffusion control during the measurements.

3.1.2. Commercial pulps

Flax, hemp, sisal, abaca, and jute pulps were kindly supplied by a Spanish company: Celulosa de Levante, S. A. Main properties of these pulps are listed in Table 13. These pulps were obtained by the soda/AQ process and bleached by ECF sequences.

Table 13. Properties of ECF bleached pulps

	Flax	Hemp	Sisal	Abaca	Jute
Degree of polymerization	1165	948	998	1928	1413
Brightness (%)	83.3	85.4	89.3	88.1	73.9
Fiber length (mm)	1.8 – 6.2	2.1 – 6.3	1.8 – 4.5	3.3 – 6.8	1.5 – 3.7
Humidity (%)	5.32	5.53	8.53	7.04	7.72

3.1.3. Chemical reagents

α-cellulose was bought from Sigma-Aldrich Company. Other chemicals were also bought from Sigma-Aldrich Company as either reagent or HPLC grades. They were used without any pretreatments.

3.2. Equipment

The stalks were chipped in a GA100 miller supplied by Black and Decker Co. The impregnation was carried out in a 2-L batch reactor made in our laboratory (Figure 15). The impregnation reactor was made of ANSI 304-L and 316 stainless steel and had a jacket connected to a commercial recycling hot water bath. At the top of the impregnation reactor, a tube connected with a nitrogen gas bottle of high pressure.

The impregnated chips were saturate-steam cooked in a stainless steel reactor of 5l made in our laboratory (Figure 16), which had two vessels. One vessel was used for a direct cooking with saturated steam at high temperature and pressure. The cooking vessel had tubes connected to the reactor to supply the steam and a jacket to prevail heating. Another vessel was used for receiving pulped materials after sudden decompression of pressure. A steam boiler with the maximum temperature 250^0C supplied saturate steam.

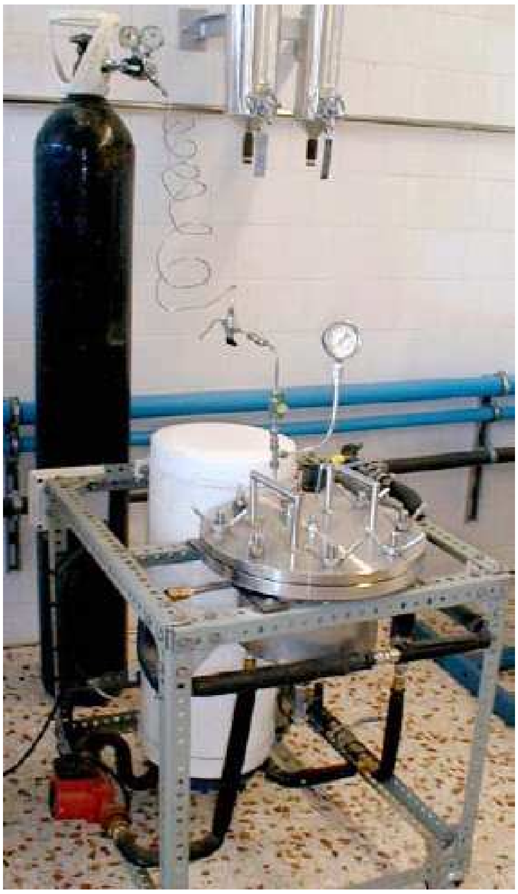

Figure 15. The impregnation equipment

Figure 16. The equipment of steam explosion

The methylation reaction was carried out in a reaction glass flask over a heat plate of Agimatic-E supply by J. P. Selecta S. A. The reaction flask was connected with a coiled reflux condenser using tap water as coolant.

The viscosities and rheological data were measured by a DIN Viscometer Visotester$^{@}$550 supplied by ThermoHaake Co. at 20^{0}C. The intrinsic viscosities were measured in an Ubbelohde viscometer combined with a 170226 Visocclock supply by SCHOTT_GERÄTE GmbH in a water bath at 25^0C for pulps or 20^0C for methylcelluloses.

The ^{13}C-NMR spectra were measured in a Gemini 300 spectrometer operating at 300MHz by using a 10 mm probe and deuterated dimethyl sulfoxide (DMSO-d_6) as solvent at 80^0C. Present spectral condition was adopted from the investigation of Takahashi et al. (1987). The spectra are obtained by using a spectral width of 24.0 kHz, a repetition time of 3s, a flip angle of 45^0 and accumulated scans of 20,000 (Takahashi et al., 1987).

The XRD measurements were obtained using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ-θ goniometer) fitted with a curved praphite diffracted - beam monochromator, a diffracted beam Soller slit, a 0.06^0 receiving slit and scintillation counter as a detector. The angular 2θ-diffraction range was between 5 and 70^0. The data were collected with an angular step of 0.05^0 at 3 seconds per step and sample rotation. Cu_{ka} radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

The apparatus of the size exclusion chromatography (SEC) combined with the high performance liquid chromatography (HPLC) was an Agilent 1100 series, which consisted of the G1311a quaternary pump, the G1322a degasser, the G1313a autosampler, the refractive index detector and the G1316a column thermostat. The Agilent chemstation software for the LC and LC/MC system was used to control the HPLC apparatus. The SEC data were analyzed with the Agilent SEC data analysis software.

3.3. Experimental processes

The process of preparation of methylcelluloses from the annual plant stalks consisted of chipping, impregnation, steam pulping, screening, TCF bleaching, mercerization, methylation, and characterization of synthesized methylcelluloses. The process of preparation of methylcelluloses from the ECF bleached pulps consisted of pretreatments, mercerization, methylation and characterization of synthesized methylcelluloses.

3.3.1. IRSP Pulping

The chips of miscanthus were impregnated in 30% sodium hydroxide solution under 15 bar nitrogen pressure at 55^0C for an hour. The chips of the spring cardoon were impregnated in 30% or 20% sodium hydroxide solutions under 15 bar nitrogen pressure at 55^0C for a hour. The chips of the summer cardoon were impregnated in 30% or 20% sodium hydroxide solutions under 15 bar nitrogen pressure at 55^0C or at ambient temperature for a hour. The chips of the eucalyptus were impregnated in 30% sodium hydroxide solution under 15 bar nitrogen pressure at 55^0C for a hour. The weight ratio of chips / liquid was adjusted for the chips to be completely immersed in the liquid. Anthraquinone (AQ) was added as 0.1% of oven-dried weighty of the chips. The impregnated chips and liquors were collected and weighed respectively. The impregnated chips were stored in a cooler at 4^0C. The residual amount of sodium hydroxide absorbed in the impregnated chips was determined by a titration method.

The maximum interval time of the impregnated chips between the impregnation and the following cooking was one day. The temperature and time of the cooking were combined into a parameter, p- factor, which was calculated by the following equation (1) (Chornet and Overend, 1988):

$$P = \log(R_o) = \log(\int_0^t \exp(\frac{T-100}{14.75}) \cdot dt) \qquad (1)$$

Where R_o: the severity of pulping, p-factor; T: the reaction temperature, ^{0}C; t: the retention time, minute.

The impregnated chips were directly cooked by the saturated steam according to a series of p-factors with varied cooking time 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 pH values were close to seven. All unbleached pulps were dried in an oven at 60^0C.

3.3.2. TCF bleaching

Pulps of miscanthus were bleached by an EPP sequence (E stands for alkaline extraction and P stands for hydrogen peroxide bleaching). The bleaching sequences for the cardoon pulps were PP or PEP. 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, pulps were collected by the vacuum filtration and washed with the distilled water. The hydrogen peroxide bleaching was performed with 3-4% consistency in 0.2M NaOH and 0.15M H_2O_2 for 1 hour at 60^0C. At the end of the bleaching, the pulp was washed by the distilled water until the pH value was close to 7 and collected by filtration. The bleached pulps were dried in an oven at 60^0C.

3.3.3. Accessibility of mercerized α-cellulose

Aldrich α-cellulose was utilized in the preliminary experiments in order to find a suitable methylation method for bleached pulps. α-cellulose was mercerized in 5%, 10%, 15%, 20%, 30%, and 40% sodium hydroxide solutions at ambient temperature and pressure for one hour. Upon the mercerization, cellulose were collected by vacuum filtration and washed several times to pH 7 with distilled water. Then mercerized celluloses were dried in an oven at 60^0C to constant weight. The iodine adsorption method was used to determine the accessibilities of celluloses (Browning, 1967; Hon and Yan, 2001).

3.3.4. Methylation of TCF bleached pulps

5 grams α-cellulose or bleached pulp (based on dry weight) was mercerized in 100 grams 40% sodium hydroxide solution for 1 hour at the room temperature (at about 20^0C). The mercerized pulp was filtered and pressed until the weight ratio of the pulp and the sodium hydroxide solution to be 0.2. Upon the filtration, the mercerized pulp, 150 ml 2-propanol, and 50 ml iodomethane were added into a flask. The methylation reaction lasted for 22 hours at 60^0C. The mercerization and methylation were repeated. At the end of methylation, the methylcellulose was collected by the vacuum filtration, neutralized with acetic acid, and washed three times by acetone and ethanol respectively. Finally, methylcellulose samples were stored in a cooler at 4^0C.

3.3.5. Pretreatments of ECF bleached pulps

Water soaking

Approximately 10 g pulp (oven dry weight) was soaked in 500 g distilled water for one hour at the room temperature (about 22^0C). The pulp was collected by filtration and dried in the air.

Mercerization

Approximately 10 g pulp (oven dry weight) was mercerized in 200 g 50% sodium hydroxide solution for one hour at the room temperature (about 22^0C) under ambient pressure. The mercerized pulp was collected by filtration and washed with distilled water until the pH value was close to seven. The mercerized pulp was dried in the air.

Preliminary mercerization

Approximately 10 g pulp (oven dry weight) was mercerized in 200 g 15% sodium hydroxide solution for ten minutes at the room temperature (about 22^0C) under the ambient pressure. The mercerized pulp was collected by filtration and pressed to a press weight ratio for the solution and pulp of 3. The mercerized pulp was kept in the air at the room temperature for four hours. The mercerized pulp was washed with distilled water until the pH value was close to seven. The mercerized pulp was dried in the air.

Mercerization under pressure

Approximately 10 g pulp (oven dry weight) was mercerized in 200 g 50% sodium hydroxide solution for one hour at room temperature (about 22^0C) under 15 bar nitrogen pressure. The mercerized pulp was collected by filtration and wash with distilled water until the pH value was close to seven. The mercerized pulp was dried in the air.

Steam explosion

The saturate steam directly heated approximately 10 g pulp (oven dry weight) in the steam explosion equipment. The temperature was quickly raised to 140^0C by the saturated steam. The temperature was kept at 140^0C for four minutes by adding a little steam at intervals. The pressure was suddenly decompressed. The pulp was exploded into the receive vessel. The steam-exploded pulp was collected by filtration and dried in the air.

3.3.6. Methylation of ECF bleached pulps

Approximately 5 g pulp (oven dry weight) was mercerized in approximately 120 g 50% NaOH solution at ambient temperature (about 22^0C) for one hour. The mercerized pulp was filtered and pressed to the weight ratio of the NaOH solution and the pulp to be 3. The mercerized pulp and 300 ml isopropanol were added to a 500 ml flask. The suspended solid and solvent was stirred for 1 hour at the room temperature (about 22^0C). The flask was installed with a condenser and placed in a water bath. 50 ml iodomethane was added into the suspended slurry. The mixed slurry was stirred for another one hour at room temperature (about 22^0C). The temperature of the water bath was raised to 60^0C and maintained for 22 hours. After this first methylation, the second mercerization and methylation were carried out to obtain a synthesized methylcellulose of higher degree of substitution.

At the end of the second methylation, the methylcellulose was collected by filtration, neutralized with acetic acid, and washed with ethanol and acetone three times respectively.

3.3.7. Fractionalization of methylcellulose

The process of fractionalization of a crude methylcellulose is shown in Figure 17. Approximately 1 g methylcellulose (oven dry weight) was added into 20 grams distilled water in a glass sample bottle and stirred for 2 hours until all fibers were separated into small pieces. The bottle was placed in a cooler at 4^0C for 24 hours in order to improve the solubility of water-soluble methylcellulose. The mixture was took out and stirred for 2 hours until its temperature was near to the room temperature. The bottle was placed into a centrifuge and centrifuged at 4000 rpm for

30 minutes. The solid was collected by filtration and washed three times with distilled water. The solid comprised the alkali soluble methylcellulose and unreacted pulp. The liquid comprised the water-soluble methylcellulose and salts. The solid was dried in the air and extracted by 4% NaOH solution. The solid, which did not dissolve in the 4% NaOH solution, was assumed unreacted pulp, which might have comprised methylcellulose of a very low degree of substitution.

The dissolved and washed liquids were collected and placed in a dialysis membrane bag. The dialysis bag was suspended in distilled water for three weeks. The dialysis purification used the Spectrum® dialysis tubing cellulose membrane bag with an average flat width of 76 mm (3.0 in.), supplied by the Spectrum Laboratories Inc. via the Sigma-Aldrich Company. Each dialysis tube bag was clamped by two 110 mm dialysis-tubing closures. The cellulose membrane could separate salts and methylcellulose with Mw of less than 12,000. The diffusion velocity was improved by stirring the distilled water. The dialysis methylcellulose was dried first in the air and then in a desiccator under vacuum.

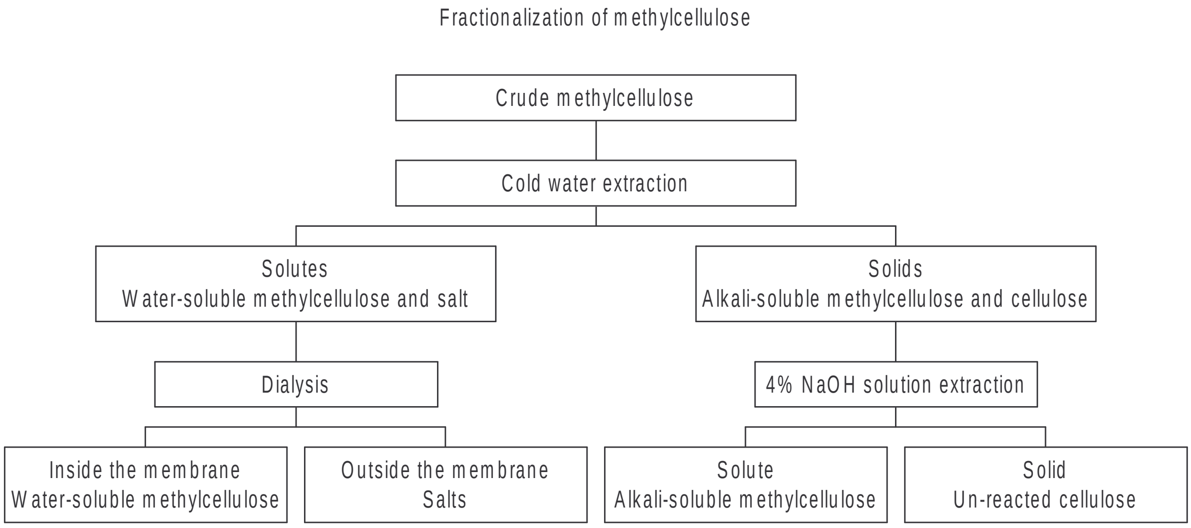

Figure 17. Fractionalization of synthesized methylcellulose

3.4. Characterization

3.4.1. Composition analysis of plant stalks

Raw materials are analyzed by following standard procedures: ASTM D 1102 – 84 for ash content, ASTM D 1111 – 84 for hot watery extractives content, modified ASTM D 1107 – 84 for ethanol / toluene organic extractives content, ASTM D 1106 for Klason lignin content, ASTM D 1104 – 56 for holocellulose and ASTM D 1103 – 60 for α-cellulose.

3.4.2. Analysis of pulps

Kappa number is determined according to TAPPI T 236 om-99. The residual lignin content is estimated by the kappa number times 0.15. The viscosity of pulps is determined by TAPPI T 230 om-99 (capillary viscometer method). The intrinsic viscosity is estimated by the Schula-Blaschke equation. The ash content was determined according to ASTM D 1102 - 84. The kappa number was determined according to TAPPI T 236 om-99. The lignin content was estimated from the kappa number. The α-cellulose was determined from its definition: α-cellulose was that part of a cellulosic material that was insoluble in 17.5% solution of sodium hydroxide at 20° C. The intrinsic viscosity of the pulps was determined according to the ISO 5351-1, 1981.

3.4.3. Determination of main monosacchrides of ECF bleached pulps by HPLC

Hydrolysis of the pulps was carried out by the procedure of determination of the Klason lignin content. 0.3 g pulp was hydrolyzed in 24.1 N H_2SO_4 solution at 30^0C for 1 hour. Then it was diluted and the hydrolysis was continued in an autoclave during 30 minutes at 120^0C.

The clear solution was collected by centrifugation and analyzed using a BIO RAD Aminex HPX-87P column (300-7.5mm) with the High Performance Liquid Chromatography (HPLC). Glucose and xylose solutions were used to calibrate.

3.4.4. Determination of accessibility

Accessibility of pulps was determined by an iodine absorption method (Hon and Yan, 2000). The iodine solution was prepared by dissolving 1 g iodine and 8 g potassium iodide into 10 ml distilled water. The saturated solution of sodium sulfate was prepared by gradually adding 250 g sodium sulfate into 750 g distilled water with continue stirring in a water bath at 25^0C. Three tenths of a gram of pulp (oven dried weight) was added to a flask. 2 ml of iodine solution was then added. The pulp and solution were thoroughly mixed with a glass rod. 100 ml of saturated solution of sodium sulfate was added into the flask. The flask was stored in the dark for 1 h. 50 ml of distilled water and several drops of 1% starch solution were added. The residual iodine in the solution was determined by titrating with 0.02N sodium thiosulfate. A blank on the original iodine solution was determined simultaneously with the same procedure. Accessibility (mg iodine / g pulp) was calculated by the following formula:

$$accessibility = (a-b)\times 2.04\times 2.54/0.3$$

Where a is the volume of the 0.02N thiosulfate solution for the blank and b is the corresponding volume for the cellulose.

3.4.5. Determination of degree of crystallinity

The XRD spectra of the pulps show a very intense pick at 22.6º, which corresponds to the crystalline region (plane 200), and other intense picks before 18.0º (Segal L, 1959).

The crystallinity index was calculated using the intensities of diffraction of the crystalline structure (plane 002, 2θ=22.6º) and of the amorphous fraction (2θ=18.0º):

$$CrI = 100\times\left(\frac{I_{002}-I_{amorphous}}{I_{002}}\right)$$

3.4.6. *Microscopic structure by SEM*

All the pulps and preliminary treated pulps were dried in the air at room temperature. Their morphological structures were viewed using a JEOl JSM-6400. A little pulp was placed onto a carbon adhesive plate, which was attached to a metal cylinder. The sample was carried out the gold metalization using a BALZERS SCD 004 sputter coater, under a pressure of 0.05mbar and 3 treatments of 30s with to 30mA and a distance of 50mm.

3.4.7. *FTIR spectra*

FTIR spectra were obtained using a JASCO FT/IR-6300 spectrometer with attenuated total reflectance (ATR). 64 scans with a resolution of 2 cm^{-1} were recorded. The wave number region ranged from 4000 to 400 cm^{-1}. Each sample was measured twice and its average value was calculated and used. The absorbance band area, which was calculated from a local baseline between adjacent peaks, were automatically calculated at the maximum absorbance found by a noise level of 0.1 using the Spectra Manager for windows 95/NT from the JASCO Corporation. The baseline was corrected automatically by the peak find tool using the Spectra Manager software.

The area ratio of band 1375 and 2900 was assigned to be the relative crystallinity index (O'Connor et al., 1958; Nelson and O’Conner, 1964; Selim et al., 1994). The area ratio of band 3300 and 2900 was assigned to be the mean hydrogen bond strength (O'Connor et al., 1958; Selim et al., 1994).

3.4.8. *Analysis of methylcellulose*

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

3.4.9. Determination of degree of substitution by ^{13}C NMR

The methylcellulose sample was dried in an oven at 105^0C until a constant weight and dissolved in the deuterated DMSO (DMSO-d6) at 80^0C. The DS of methylcellulose was determined by the ^{13}C nuclear magnetic resonance spectroscopy in the dimethyl sulphoxide solution at 80^0C during 6 hours for each methylcellulose sample.

3.4.10. Determination of molecular weights of water-soluble methylcellulose

Solutions for chromatographic analyses were prepared quantitatively by distilled water extraction. The concentration of water-soluble methylcellulose had to be in the range 0.2-0.4% and this was ensured by weighing a certain amount of methylcellulose on an electric balance. The weighed methylcellulose was then transferred into a 10 ml sample glass vial and 9 ml distilled water was added. The solution was stirred for two hours at room temperature (about 20^0C) and then the vial was placed in a refrigerator at 4^0C and stored for 24 hours. After this time, the vial was taken out of the refrigerator and the solution was stirred for another two hours at room temperature (at 20^0C). The suspended solution in the vial was centrifuged at 4000 rpm for 30 minutes. The upper clear liquid was removed with a syringe and filtered using a nylon membrane syringe filter of 13 mm ϕ with a diameter pore 0.2 μm. The filtered solution was injected into a 1.5 ml HPLC sample vial for SEC analysis.

A modified SEC condition was used (Keary, 2001). The eluant was 0.05 m NaCl solution, which was prepared with distilled water and filtered with an Albet® polytetrafluoroethylene (PTFE) membrane filter of 47 mm ϕ and a pore diameter of 0.2 μm. The eluant was degassed by an on-line degassing system, the G1322a degasser. The flow rate was 1 ml/min. The temperature of the G1316a column thermostat was set at 25^0C. Samples were automatically injected using the G1313a autosampler. Two columns were used in series: a size exclusion chromatography column (Tosohaas, Tsk Gel G 3000 Pwxl, 7.8 mm id ×30 cm) and a guard column (Tosohaas, Tsk column guard Pwxl).

4. Results and discussion

4.1. Introduction

In present investigation, methylcelluloses were prepared from some annual plants via a novel facile methylation method, which was developed in our laboratory (Ye and Farriol, 2005a). New raw materials of methylcelluloses were investigated in order to substitute conventional materials: cotton and wood dissolving pulps.

Two annual plants (miscanthus sinensis and cardoon), and juvenile eucalyptus of two years old were used to prepare methylcelluloses. The whole process of the preparation of methylcelluloses consisted of impregnation, rapid steam pulping, TCF bleaching, mercerization, and methylation. In the preparation of methylcellulose, the factors that influenced the properties of the synthesized methylcelluloses were investigated and discussed.

Miscanthus, cardoon, and eucalyptus are usually planted and cultivated in order to produce energy or to provide for domestic applications because of their fast growth, and low request of soil condition (Nick and Emmanuel, 2000; Ye et al., 2005b). Only in recent years, the cardoon and miscanthus stalks are investigated and evaluated for pulping and papermaking (Fernandez and Curt, 1995; Bouchra et al., 1997; Antunes et al., 2000; Jorge et al., 2001). To my knowledge, no former research has been done for the producation of methylcelluloses from the annual miscanthus, the annual cardoon, and the juvenile eucalyptus. It is the first time to investigate the preparation of methylcelluloses from the annual miscanthus, and the annual cardoon, and the annual eucalyptus in this dissertation.

The commercial ECF bleached jute, flax, sisal, hemp, and abaca pulps were used to prepare methylcelluloses, and to investigate their accessibilities and reactivities in order to improve the properties of the synthesized methylcelluloses. Jute, flax, sisal, hemp and abaca now are receiving more attention in the research of pulping, papermaking, and cellulose derivatization because they have lower lignin contents, higher yields of cellulose (Han and Rowell, 1996) than woods have in the countries where the forest is limit and these plants are available in sufficient quantity (Brandlt, 1986). To my knowledge, no former scientific papers were published, in which the authors investigated and discussed the preparation of methylcelluloses from the ECF bleached pulps of jute, flax, sisal, hemp, and abaca. The influencing factors of molecular weights and degrees of substitution have never been investigated in a whole process ranging from pulping to methylation.

In conclusion, the methylcelluloses were for the first time prepared from new alternative resources by a novel facile methylation method. The preparation conditions and properties of synthesized methylcelluloses were researched. The synthesized methylcelluloses had similar properties and applications as commercial methylcelluloses. It is valuable and viable to synthesize methylcelluloses from low-valued biomass materials. Therefore, the low-value annual plants are upgraded and have a new alternative application as the resources to produce methylcellulose.

4.2. A novel facile methylation method

α-Cellulose was mercerized in 5%, 10%, 15%, 20%, 30%, and 40% NaOH and soaked in distilled water for 1 hour, respectively. The accessibilities of α-celluloses after these pretreatments are shown in Figure 18. The accessibilities increased considerably after mercerization in sodium hydroxide solutions with increasing alkali concentrations. The best result was obtained in 15% NaOH solution. However, after mercerization in 15 % NaOH, there were still some crystalline regions in the cellulose. Hence, excess sodium hydroxide solution should be retained after mercerization so that alkali cellulose can completely form during methylation.

The FTIR spectra of these pretreated celluloses are shown in Figure 19, 20 and 21. It is well known, the mercerization of cellulose degrades the cellulose, ruptures the cellulose crystals, and separates the aggregated fibrils (Ye and Farriol, 2005b). Comparison to the FTIR spectra of original pulps and mercerized pulps of a same species, the area ratios of band 1375 and 2900, as well as the area ratios of band 3300 and 2900, are changed by the pretreatments or mercerization. The relative crystalline index of each mercerized α-cellulose decreased, which meant more accessible amorphous cellulose was created (Ye and Farriol, 2005b). The mean hydrogen bond strength of each mercerized α-cellulose also decreased, which meant a part of aggregated fibrils were ruptured and some crystalline celluloses were transformed to be amorphous celluloses (Krassig, 1993). Thus, the accessibilities and reactivities of celluloses were improved by these mercerization. The water soaking can decrease the hydrogen bond strength (Ye and Farriol, 2005b). Thus, the water soaking pretreatment increased the accessibility and reactivity of cellulose. As the concentration of NaOH solution increased, the relative crystalline indexes and mean hydrogen bond strengths decreased. These data indicated a higher concentration of NaOH had a better effect of mercerization of cellulose.

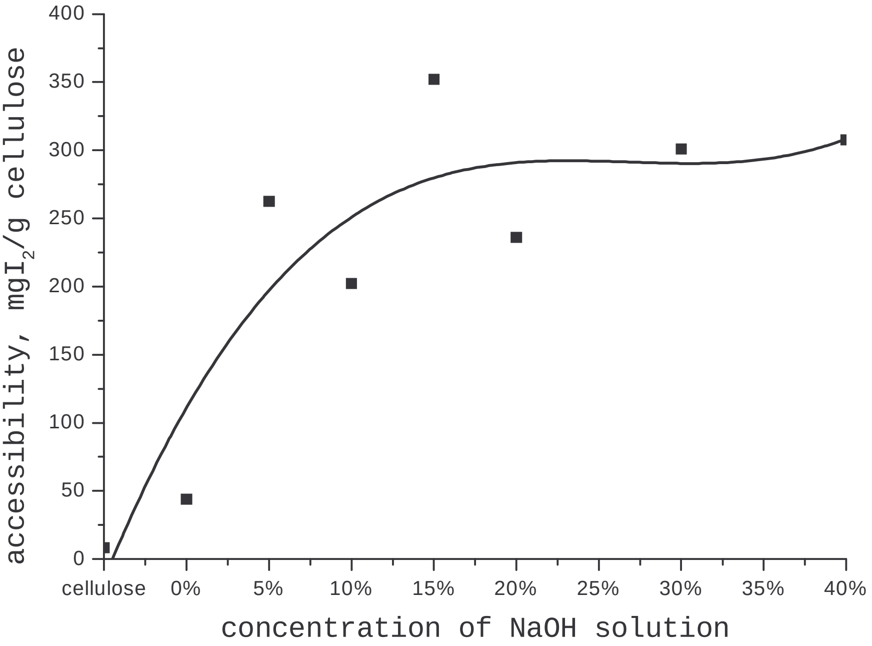

Figure 18. Accessibility of mercerized cellulose

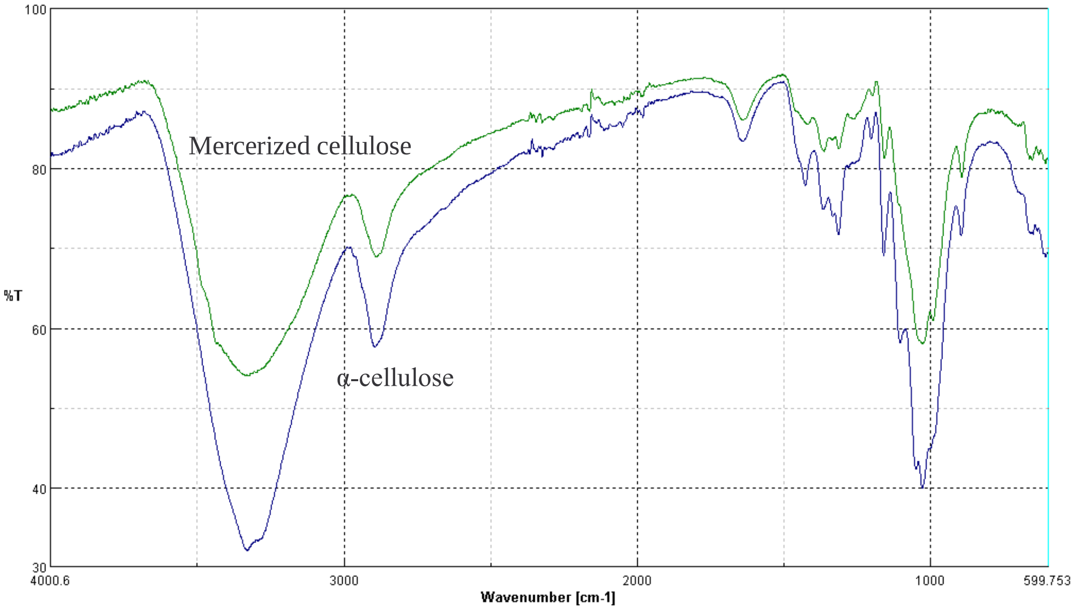

Figure 19. FTIR spectra of α-cellulose and α-cellulose treated by 15% NaOH

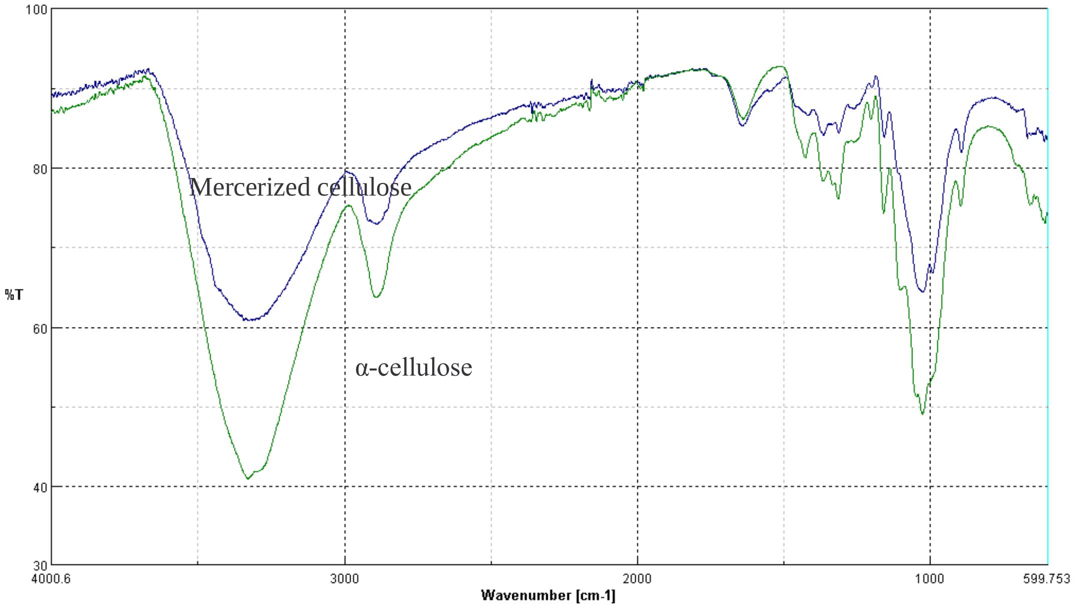

Figure 20. FTIR spectra of α-cellulose treated by 30% NaOH and water soaking

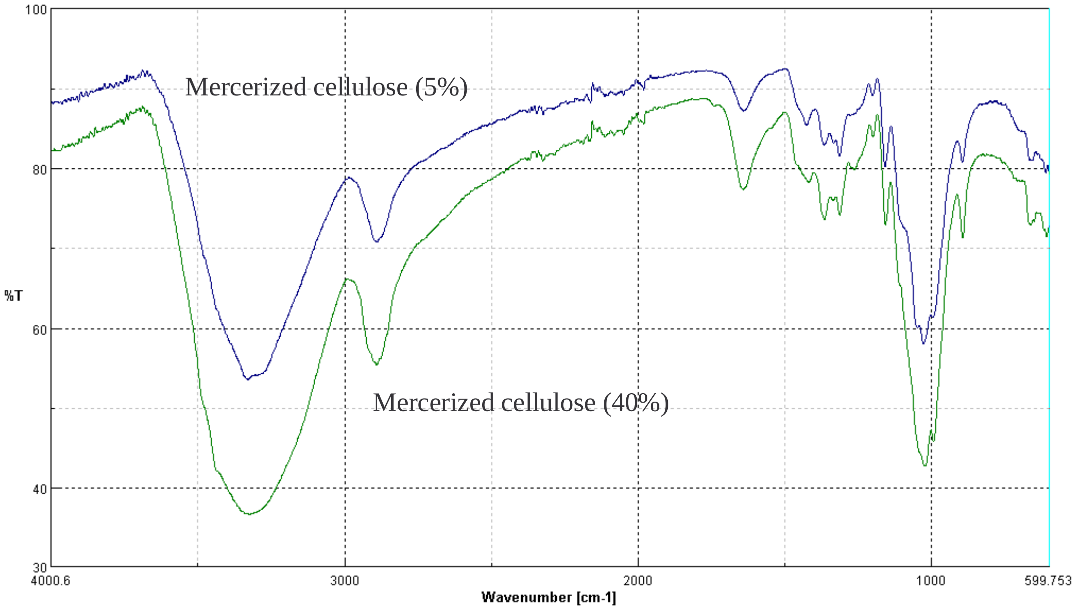

Figure 21. FTIR spectra of α-cellulose treated by 5% and 40% NaOH

α-Cellulose was mercerized in 15% and 40% sodium hydroxide solutions, respectively. Then mercerized cellulose was collected by vacuum filtration and methylated with 50ml iodomethane at 60^0C for 22h in 2-propanol slurry. The obtained methylcelluloses were compared only for their solubilities in dimethyl sulphoxide. It was assumed that methylcellulose can be completely dissolved in DMSO when its degree of substitution is between 0.6 and 2.0 (Croon and Manley, 1963). The methylcellulose prepared from 40% sodium hydroxide solution completely dissolved in DMSO solution. However, the methylcellulose prepared from 15% sodium hydroxide solution only partly dissolved. These results showed that 40% sodium hydroxide solution was better for mercerization than 15% sodium hydroxide solution.

5g dry weight of α-cellulose was 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 better reaction conditions. These results are listed below in Table 14. Water-soluble contents increased as the volumes of iodomethane increased. All samples were soluble in 4% NaOH solution at 20^0C, which meant that they were alkali-soluble methylcelluloses and all the crystalline cellulose participated in the methylation reaction. All samples were partially soluble in distilled water at 20^0C, which meant that separation methods such as extraction, dialysis, or membrane separation were required to obtain water-soluble methylcelluloses.

In order to empirically estimate a intrinsic viscosity of methylcellulose from the viscosity in alkali solutions, the viscosities and intrinsic viscosities of the methylcelluloses were measured in 4% NaOH solution at 20^0C. The concentration of methylcellulose was 0.5 %. The empirical equation was expressed as formula 1.

$$viscosity = K \times intrinsic\_viscosity^{A} \qquad (1)$$

Where *viscosity* was the viscosity of 0.5 % concentration of methylcellulose in 4% NaOH solution at 20^0C, K and A were constants, intrinsic_viscosity was the intrinsic viscosity measured in 4% NaOH solution at 20^0C.

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 methylcelluloses in 4% NaOH solution can be estimated as formula 2.

$$viscosity = 0.065 \times intrinsic\_viscosity^{0.80} \qquad (2)$$

The results of the degrees of substitution of methylcelluloses are listed in Table 15. The average degrees of substitution increased as the iodomethane volumes increased. The data showed that substitution at the 2-OH group was easier than at the 3-OH and 6-OH group. The substitution at the 3-OH group was easier than or the same as at the 6-OH group. As the molar ratio of iodomethane and anhydroglucose increased, the value of substitution at the 6-OH group increased more than at the 3-OH group, which indicated that an increase in methylation reagents led to a better methylation reaction and better substituent distribution on the anhydroglucose unit of cellulose (Croon and Manley, 1963). This better substitution led to better solubility in a variety of solvents (Croon and Manley, 1963).

Figure 22 shows the spectra of α-cellulose and MD23 that was synthesized from α-cellulose. The most significant difference of these two FTIR spectra was the methoxyl group. The spectrum of MD23 had a 2830 cm^{-1} bond, which indicated some hydroxyl group were substituted to be the methoxyl group. Thus, the FTIR spectrum demonstrated the obtained product was methylcellulose.

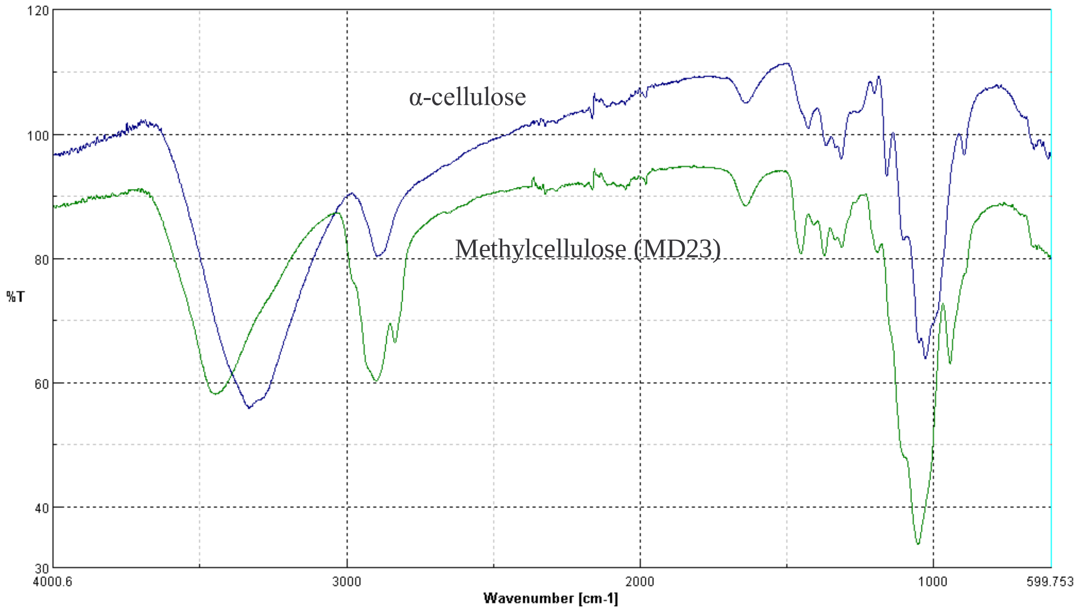

Figure 22. FTIR spectra of α-cellulose and MD23

Table 14. Solubility and viscosity 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.

Table 15. DS of α-cellulose methylcelluloses

Methylcellulose	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

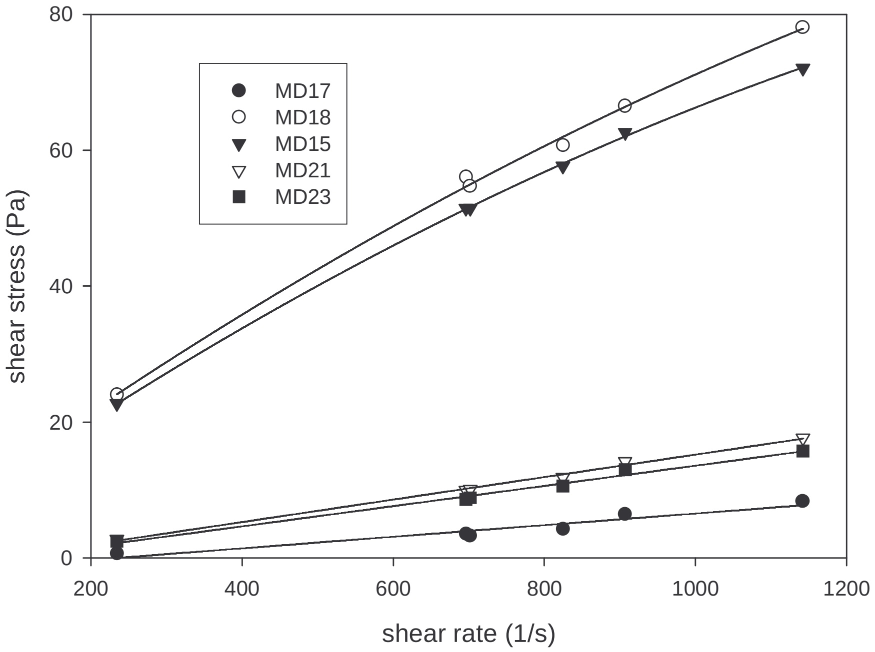

Figure 23. Rheological properties of α-cellulose methylcelluloses in 1 % DMSO solutions

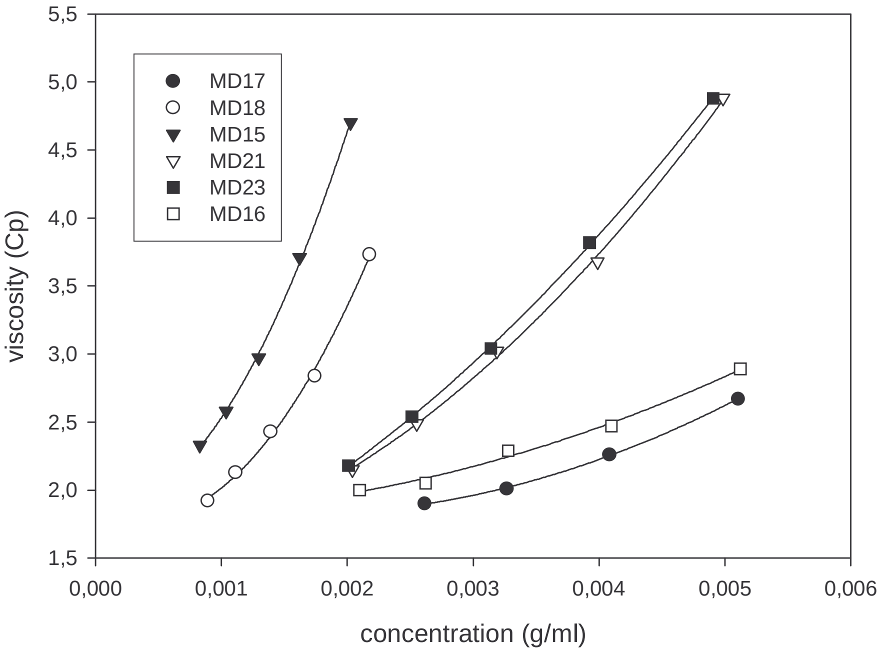

Figure 24. Dilute solution properties of α–cellulose methylcelluloses in 4% NaOH solutions

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 Figure 23. The solution properties in 1% DMSO solutions were quite different and had different molecular weights. All the samples with lower intrinsic viscosities (MD17, MD21 and MD23) seemed to be of the Newtonian type with correspondent viscosity and shear stress according to their molecular weights or intrinsic viscosities. The rheological data of samples with high molecular weights (MD18 and MD15) seemed to be pseudoplastic. The dilute solution properties are shown in Figure 24. The viscosities of all the samples increased with the increase of solution concentrations. The molecules with higher molecular weights had higher viscosities even at very low concentrations.

Considering all the above preliminary cellulose methylation, the best conditions for synthesizing methylcellulose were mercerization with 40% NaOH solution and reaction with 50 ml iodomethane per 5g cellulose at 60^0C in 150 ml 2-propanol slurry for 22 hours.

4.3. Preparation of methylcelluloses from miscanthus, cardoon, and eucalyptus

4.3.1. Chemical compositions

Table 16. Chemical compositions of miscanthus, cardoon, and eucalyptus

Plants	Miscanthus (%)	Spring cardoon (%)	Eucalyptus (%)
Ash	0.7	5.0	1.5
Water extractives	3.1	26.7	7.6
Organic extractives	9.1	5.1	0.5
Klason lignin	19.9	13.9	25.4
Holocellulose	72.5	48.3	71.0
α-Cellulose	42.2	24.0	48.6

Chemical compositions based on oven-dried weight (ODW) of original materials are listed in Table 16. Miscanthus had the highest holocellulose content, the highest organic extractive content, and the lowest ash content of these three plants. The water extractive content of the spring cardoon was 26.7% because the spring cardoon was harvested with green capitula, leaves and stalks. Thus, many water-soluble materials coexisted in the spring cardoon stalks. The spring cardoon had the highest ash content, the lowest lignin content, the lowest holocellulose content, and the lowest α-cellulose content. These data indicated the leaves and capitula of the spring cardoon must be eliminated before the subsequent pulping. The sum of water and organic extractive contents of the eucalyptus was the lowest. The eucalyptus had the highest lignin content, the lowest organic extractives content, and the highest α-cellulose content. These results showed the miscanthus, the spring cardoon and the juvenile eucalyptus had potential to be alternative raw materials of paper, pulp, and cellulose derivatives. The pulping severities of miscanthus and cardoon must be lower than that of eucalyptus because eucalyptus has higher lignin content.

4.3.2. Pulping

The pulping in our study used the IRSP process, which comprised two steps: impregnation and rapid steam pulping.

4.3.2.1. Impregnation

Table 17. Parameters and results of impregnation

Material	AQ (%)	NaOH concentration (%)	Retention time (Hour)	Temperature (^0C)	Residual alkali* (%)
Miscanthus	0.1	30	2	55	44.6
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

*Based on the initial NaOH charge.

Designed impregnation parameters and residual alkali in the impregnated fibers are shown in Table 17. 44.6% of NaOH was absorbed in the miscanthus stalks. When the miscanthus chips, the spring cardoon chips, and the eucalyptus chips were impregnated at a same impregnation condition, the eucalyptus chips absorbed the lowest amount of alkali, and the spring cardoon chips absorbed the highest amount of alkali. The highest amount of absorption of alkali of the cardoon chips indicated the spring cardoon chips were more porous than the eucalyptus and miscanthus chips, which also meant that the pulping severities of cardoon should be lower than that of eucalyptus and miscanthus.

The residual NaOH in the impregnated chips of cardoon increased with the increase of impregnation time and the concentration of the sodium hydroxide solution. When the concentration of NaOH solution increased from 20% to 30%, the residual NaOH increased by 46%. When the retention time increased from 1 to 2 hours, the residual NaOH increased by 53%. This residual NaOH may be considered as the main pulping chemical in the following cooking with saturate steam. The high pressure of 15 bars, and the intermediate temperature (60^0C) facilitated the penetration and diffusion of NaOH solution in the plant stalks. Therefore, the impregnation time was reduced to 2 hours while the traditional impregnation needed 24 hours at ambient pressure (Barba, 2002). The better impregnation condition for the spring cardoon chips may be in the 30% sodium hydroxide solution under 15 bars pressure for 2 hours at 55^0C.

4.3.2.2. Rapid steam pulping

Steam pulping parameters and results are shown in Table 18. The kappa numbers, yields and lignin contents decreased with the increasing of p-factors, which demonstrated the p-factor was a main factor of rapid steam pulping process. Their kappa numbers of miscanthus pulps ranged from 6.5 to 14.1, which meant low lignin contents of pulps. After the impregnation and rapid steam pulping, most of lignin of stalks was eliminated. These yields of miscanthus pulp were nearly 60% and relatively higher than usual chemical pulping (Han and Rowell, 1996). What is more important was that these miscanthus pulps almost had no rejects, which had advantage of reducing screening equipment and cost. The intrinsic viscosities of miscanthus pulps ranged from 1183 ml/g to 737 ml/g, which were suitable for further application for paper, board, and dissolving pulps (Balser et al., 1986; Brandt, 1986).

Because of lower lignin content and porous stalks, the spring cardoon was pulped with the lowest pulping severities. The p-factors of the spring cardoon pulps were same (2.96) although they were impregnated in different conditions. The cardoon pulp had a higher intrinsic viscosity when its chip was impregnated in a lower concentration of NaOH solution, which demonstrated NaOH has a considerable degradation during the impregnation. Since the impregnation time of the chip increased, the intrinsic viscosity of cardoon pulp decreased. The spring cardoon chips underwent less impregnation conditions and steam pulping severities; therefore, their pulps had higher kappa numbers and lignin contents. The yields of the spring cardoon pulps were the lowest.

The intrinsic viscosities of the eucalyptus pulps were lower than the spring cardoon pulps because the eucalyptus chips were cooked by higher pulping severities. The eucalyptus was the most easily to be pulped because its pulps had lower kappa numbers and lignin contents than that of miscanthus and cardoon.

Table 18. Steam pulping results of miscanthus, cardoon and eucalyptus

Material	Time (min.)	Temperature (^{0}C)	P factor	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g, 25^{0}C)
Miscanthus 1	4	180	2.96	14.1	58.3	2.12	1183
Miscanthus 2	8	180	3.26	9.3	57.2	1.40	957
Miscanthus 3	16	180	3.53	8.3	56.3	1.25	864
Miscanthus 4	25	180	4.06	6.5	55.8	0.98	737
Cardoon 1	4	180	2.96	30.4	21.9	4.56	1287
Cardoon 2	4	180	2.96	30.9	25.1	4.64	1305
Cardoon 3	4	180	2.96	23.8	23.7	3.57	1163
Cardoon 4	4	180	2.96	28.6	24.7	4.29	1077
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

The cardoon and miscanthus stalks in our study had looser fiber structures than the eucalyptus stalks had. Thus, the pulping severities of cardoon and miscanthus stalks were lower than that of the eucalyptus stalks. High quality pulps of cardoon and miscanthus were prepared. The eucalyptus stalks were easily pulped to lower kappa numbers. Cardoon and miscanthus are potential resources of cellulose, like traditional eucalyptus.

4.3.3. TCF bleaching

Bleaching results are listed in Table 19. Bleached pulps of low lignin contents were obtained by these TCF bleaching sequences. Properties of bleached pulps were strong influenced by the pulping condition when the bleaching condition was same for miscanthus pulps. The kappa numbers, yields, lignin contents, and intrinsic viscosities decreased with the increasing of pulping severities. Kappa numbers of miscanthus TCF bleached pulps ranged from 3.1 to 7.0 and were low although peroxide was not a highly active bleaching chemical (Patt et al., 1986). The lignin contents of miscanthus TCF bleached pulps were lower than 1.1%. The yields of miscanthus TCF bleached pulps were almost over 80%. The intrinsic viscosity values of miscanthus TCF bleached pulps ranged from 414 to 727 ml/g, which were sufficient for cellulose derivation after three stages of alkaline treatments (impregnation, steam pulping and bleaching). All these bleaching results showed this TCF bleaching sequence, EPP, was effective and feasible for miscanthus pulps produced by the IRSP process (Ye et al., 2005b).

Bleached pulps of the spring cardoon had higher kappa numbers than summer cardoon pulps. The spring cardoon pulps seemed to be more difficult to be bleached than summer cardoon pulps, which indicated the harvest time of cardoon was an important factor for its pulping and bleaching. The most interesting phenomena were the summer cardoon pulps that could be bleached to the lowest kappa number although its chip was cooked by the lowest pulping severity with a lowest p-factor. The leaves and capitula of summer cardoon stalks were eliminated before the impregnation and steam pulping. This indicated the removal of leaves and capitula could improve the quality of bleached pulps of the cardoon, and the bleachability of these pulps.

Table 19. Bleaching results of miscanthus, cardoon and eucalyptus pulps

Material	P-factor	Method	Kappa number	Yield (%)	Lignin (%)	Intrinsic viscosity (ml/g, 25^0C)
Miscanthus 1	2.96	EPP	7.0	85.7	1.05	727
Miscanthus 2	3.26	EPP	4.6	84.2	0.69	601
Miscanthus 3	3.53	EPP	4.5	81.3	0.68	514
Miscanthus 4	4.06	EPP	3.1	78.6	0.47	414
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*	2.96	PP	2.1	84.9	0.32	729.6
Cardoon 6*	2.66	PP	3.5	74.8	0.53	720.4
Cardoon 7*	2.66	PP	1.4	76.6	0.21	636.6
Cardoon 8*	2.66	PP	1.4	78.5	0.21	643.2
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

*Pulp of summer cardoon.

The eucalyptus pulps were more difficult to be bleached than the cardoon and miscanthus pulps although their unbleached pulps had lower kappa numbers. The yields of the eucalyptus pulps were higher than that of the cardoon and miscanthus pulps, which indicated the cardoon and miscanthus pulp was easier to be degraded than the eucalyptus pulp. The viscosities of the eucalyptus pulps were lower than that of the cardoon pulps.

Although cardoon pulps were produced by lower P-factors, they were bleached to pulps that had the highest intrinsic viscosities and lowest kappa numbers of all the pulps of these three plants. This might be because cardoon fibers have more voids in their stalks and pulps. Eucalyptus pulps had lower intrinsic viscosities and kappa numbers than miscanthus pulps because of higher pulping severities. Miscanthus, eucalyptus and cardoon bleached pulps had very low lignin contents, which showed most of lignin was removed after the TCF bleaching process. These results showed high quality bleached pulps could be produced by the IRSP process combined with the proper TCF bleaching sequence for the miscanthus, cardoon, and eucalyptus chips (Balser et al., 1986; Brandt, 1986). The comparison of the results of pulping and bleaching show that excellent bleached cardoon pulps can be produced at low temperatures and short cooking times, which saves a lot energy. Miscanthus can also be used to prepare very good bleached pulps. Miscanthus and cardoon can substitute wood and become new sources of industrial cellulose.

4.3.4. Methylation of TCF bleached pulps

4.3.4.1. Methylation of miscanthus pulps

The methylation conditions and results are listed in Table 20. Water-soluble contents of miscanthus methylcelluloses increased as the cooking time increased. Four 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 had participated in the methylation. All the samples were partially soluble in water, which meant that further separation was needed to purify the methylcelluloses. The viscosities increased as the cooking time increased in 4% NaOH solution. The Table 20 shows that all the yields of alkali soluble methylcelluloses were very high. The yields of water-soluble methylcelluloses, however, were lower. Table 20 shows that methylcellulose yields, contents, and solubility can be improved if the cooking time or pulping severity is increased.

In order to empirically estimate the intrinsic viscosity from the viscosity in alkali solutions, the viscosities and intrinsic viscosities of miscanthus methylcelluloses were measured in 4% NaOH solution at 20^0C. The concentration of methylcelluloses for measuring viscosity was 2%. The empirical equation was expressed as formula 1 above. 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 methylcelluloses in 4% NaOH solution at 20^0C can be estimated as formula 3.

$$viscosity = 0.00082 \times intrinsic\_viscosity^{2.01} \qquad (3)$$

Figure 25 shows a NMR spectrum of miscanthus methylcellulose (MD26), in which the methylated hydroxyl groups are shown (Takahashi et al., 1987). Table 21 shows the DS of methylcelluloses prepared from miscanthus. It can be seen that miscanthus pulps were more difficult to synthesize than commercial α-cellulose. This may be due to the existence of trace lignin and the special fibril structure (Ye and Farriol, 2005). Methylation was easier for these miscanthus pulps that contained less trace lignin and were pulped by a higher pulping severity, p-factor.

The methylation was easier at the 2-OH group than other OH groups. As the steam explosion retention time increased, so did the substitution value or DS value at all OH groups. Hence, the average total DS increased. For samples that had a lower total DS value (less than 1.00), DS values at the 6-OH group were higher than the values at the 3-OH group. For samples that had intermediate total DS values, DS values at the 6-OH group were very nearly the same as the values at the 3-OH group. For the sample with the highest total DS value, the DS value at the 6-OH group was higher than the value at the 3-OH group. The DS value at the 3-OH group was lower than at the 2-OH group because of the blocking effect of the vicinal 2-OH group.

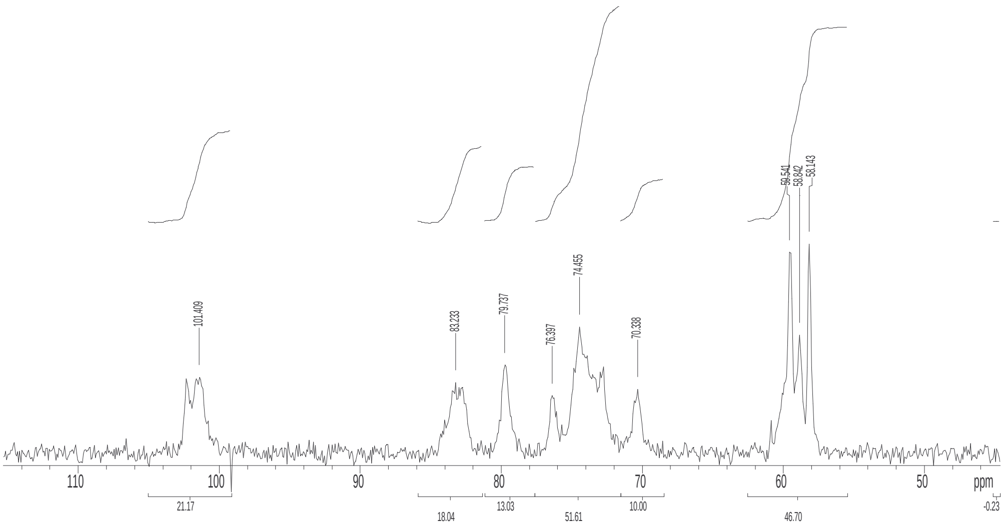

Figure 25. ^{13}C-NMR spectrum of MD26

Their rheological figures are plotted in Figure 26 and 27 in 4% NaOH solution and water at 20^{0}C, respectively. A15 is a commercial methylcellulose from DOW. Another commercial sample was bought from Aldrich with an average molecular weight of 14,000. These two samples were not pretreated and were dissolved in distilled water at 20^{0}C. The data show that their curve tendencies were similar although their viscosity values and substituted patterns were different. All these rheological data seemed to increase linearly to be Newtonian solutions. This indicated that the 4% NaOH solution may be a true solvent for low molecular weight methylcelluloses with a low degree of substitution (Croon and Manley, 1963). These phenomena demonstrate that the properties of methylcelluloses prepared from miscanthus are similar to those of commercial methylcelluloses.

Table 20. Methylation conditions and results of miscanthus 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
2% solution in 4% NaOH (mPas)	4.48	20.6	4.48	165	94.4*
Intrinsic viscosity (ml/g)	65.5	155.3	84.1	435.5	210.3

*: 2% in distilled water.

Table 21. DS of miscanthus methylcelluloses

Methylcellulose	Steam explosion time (minutes)	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*	0.67	0.38	0.47	1.52

*: higher volume of iodomethane in methylation.

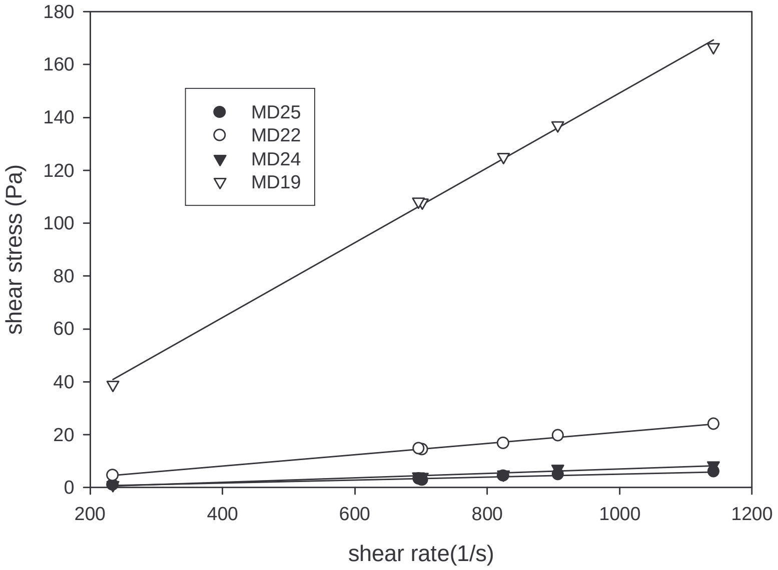

Figure 26. Rheological properties of 2% miscanthus methylcelluloses in 4% NaOH solution

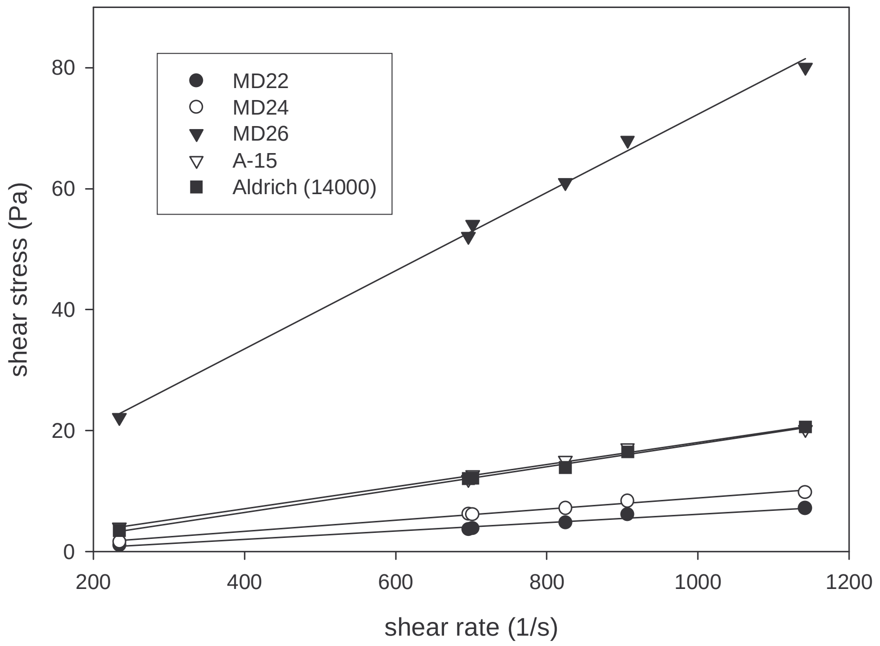

Figure 27. Rheological properties of 2% miscanthus methylcelluloses in aqueous solutions

Each prepared miscanthus methylcellulose was crude — a mixture of alkali-soluble and water-soluble methylcelluloses, which was due to the heterogeneous methylation. For textile treatments, synthesized methylcelluloses would need further purification with 4% NaOH solution to produce high-yield alkali-soluble methylcelluloses. For aqueous applications, synthesized methylcelluloses would need further purification with water to increase its DS and its solubility. Methylcelluloses synthesized from miscanthus had a DS ranging from 0.46 to 1.52 and intrinsic viscosities ranging from 65.5 to 210.3 ml/g. These low DS and small intrinsic viscosities mean that methylcelluloses synthesized from miscanthus in our study could be used as a drug component or additives, a food component, a cement additives, and other related applications (Brandt, 1986).

4.3.4.2. Methylation of cardoon and eucalyptus pulps

The yields of methylcelluloses of cardoon and eucalyptus are listed in Table 22. We can see that the methylcellulose of the summer cardoon had lower water-soluble contents than the methylcelluloses of the spring cardoon and eucalyptus. The eucalyptus methylcelluloses had higher water-soluble contents than the cardoon methylcelluloses. Most of the alkali soluble contents of methylcelluloses were over 95%. The methylcelluloses of the spring cardoon had the lowest alkali soluble contents of all the methylcellulose samples. It seems that the eucalyptus 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 polymerization. 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 methylcelluloses.

Figure 28 and Figure 29 show two NMR spectra of eucalyptus methylcellulose (MD37) and cardoon methylcellulose (MD30), in which the methylated hydroxyl groups are shown. The DS of methylcelluloses are shown in Table 23. Most of spring cardoon methylcelluloses 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 accessibilities. although the pulping severities of eucalyptus were higher than that of spring cardoon, the eucalyptus methylcelluloses had lower DS. This shows that species is a deciding factor for the synthesis of methylcelluloses, 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 of the second OH group were bigger than that of 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.

Viscosities in both DMSO and 4% NaOH solution are shown in Tables 24 and 25. Summer cardoon methylcelluloses had higher viscosities than the spring cardoon methylcelluloses in two solvents because the spring cardoon was subjected to higher pulping severities. When the p-factor increased, the viscosity of eucalyptus methylcelluloses in DMSO and 4% NaOH solution decreased. This also shows that the p-factor is an important parameter for the synthesis of methylcelluloses.

The intrinsic viscosities of the cardoon methylcelluloses in the 4% NaOH solution are shown in Table 26 and the intrinsic viscosities of the eucalyptus methylcelluloses are shown in Table 27. The summer and spring stalks could be used to prepare methylcelluloses with similar intrinsic viscosities, such as cardoon-4, cardoon-6, and cardoon-7. The eucalyptus methylcelluloses had lower intrinsic viscosities than the cardoon methylcelluloses, which may have been due to the higher pulping severity of the eucalyptus chips. The intrinsic viscosities in the DMSO solution were higher than that in the 4% NaOH solution.

The solution properties of the cardoon methylcelluloses are shown in Figures 30 and 31 and those of the eucalyptus methylcelluloses are shown in Figures 32 and 33. 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 although they had different viscosities and substituted patterns.

The application of methylcelluloses 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 methylcelluloses due to the heterogeneous methylation. For textile treatments, synthesized methylcelluloses would need further purification with 4% NaOH solution to produce high-yield alkali-soluble methylcelluloses. For aqueous applications, synthesized methylcelluloses would need further purification with water to increase its DS and its solubility. Commercial methylcelluloses are usually produced with a DS ranging from 1.4 to 1.9 and a viscosity ranging from 10 to 15000 mPas of 2% aqueous solutions at 20ºC and 20 rpm (http://www.herc.com). Methylcelluloses synthesized 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 methylcelluloses synthesized from cardoon could be used as a viscosity controller. Methylcelluloses synthesized 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 methylcelluloses synthesized from eucalyptus could be used as a drug component or additives such as a low viscosity biopolymers (Kokubo et al., 1998).

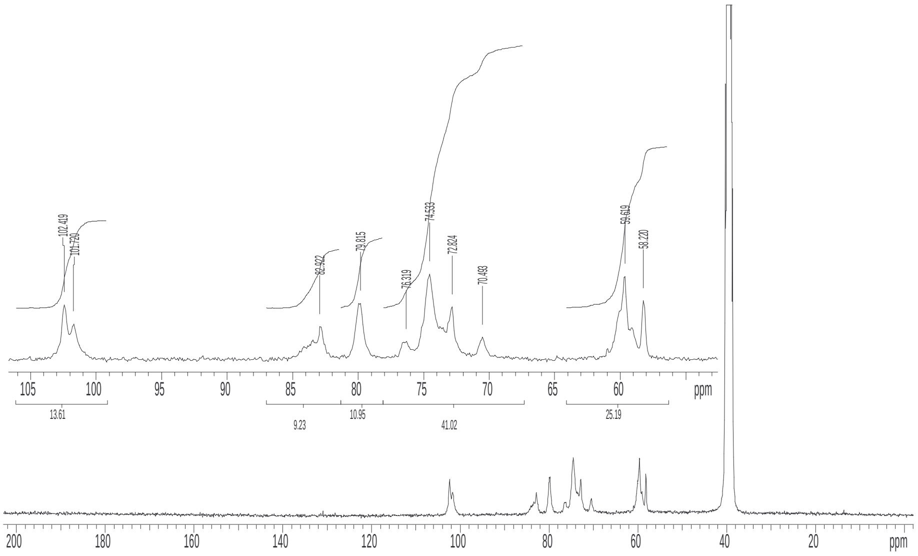

Figure 28. The ^{13}C NMR spectrum of MD37 of eucalyptus

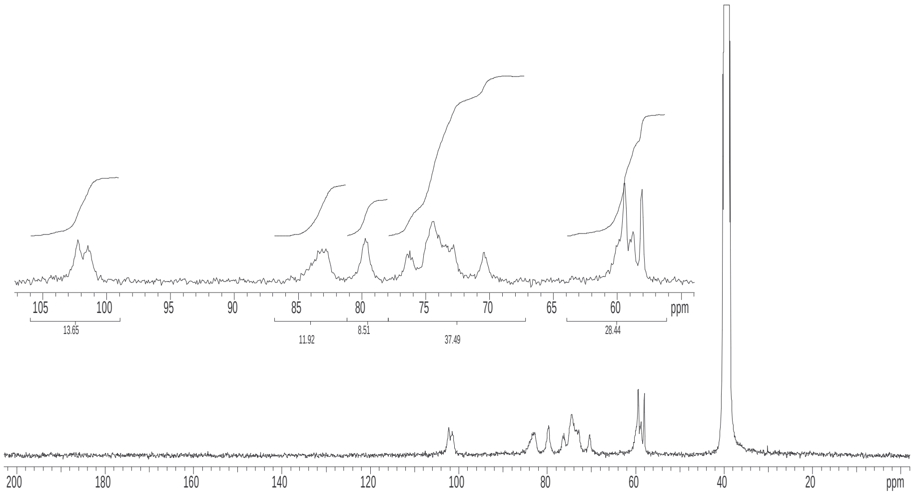

Figure 29. The ^{13}C NMR spectrum of MD30 of cardoon

Table 22. Yields of methylcelluloses prepared from cardoon and eucalyptus

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

Table 23. DS of cardoon and eucalyptus methylcelluloses

Material	Methylcellulose	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 24. Viscosities of cardoon methylcelluloses

Material	Methylcellulose	0.5% in 4% NaOH (mPas, 20^0C)	1% in DMSO (mPas, 20^0C)
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 25. Viscosities of eucalyptus methylcelluloses

Material	Methylcellulose	0.5% in DMSO (mPas, 20^0C)	1% in 4% NaOH (mPas, 20^0C)
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

Table 26. Intrinsic viscosities of cardoon methylcelluloses

Material	Methylcellulose	4% NaOH (ml/g, 20^0C)
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 27. Intrinsic viscosities of eucalyptus methylcelluloses

Material	Methylcellulose	DMSO (ml/g, 20^0C)	4% NaOH (ml/g, 20^0C)
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

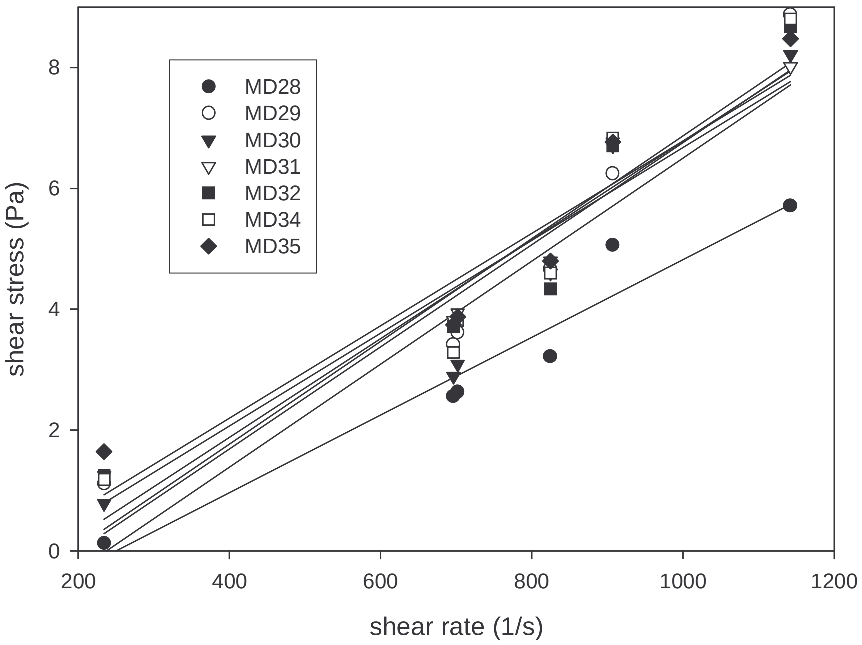

Figure 30. Rheological property of 0.5% cardoon methylcelluloses in 4% NaOH solutions

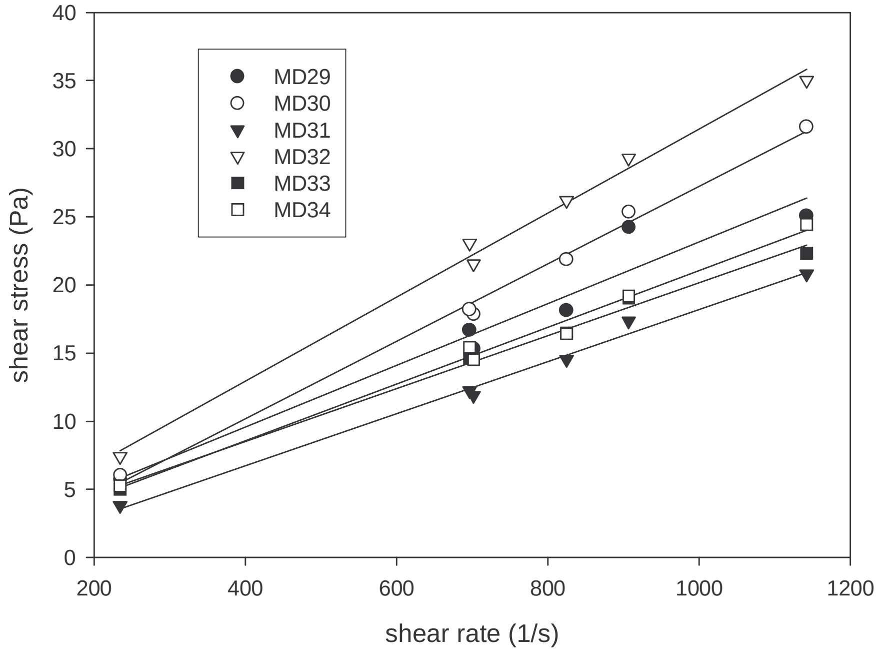

Figure 31. Rheological property of 1% cardoon methylcelluloses in DMSO solutions

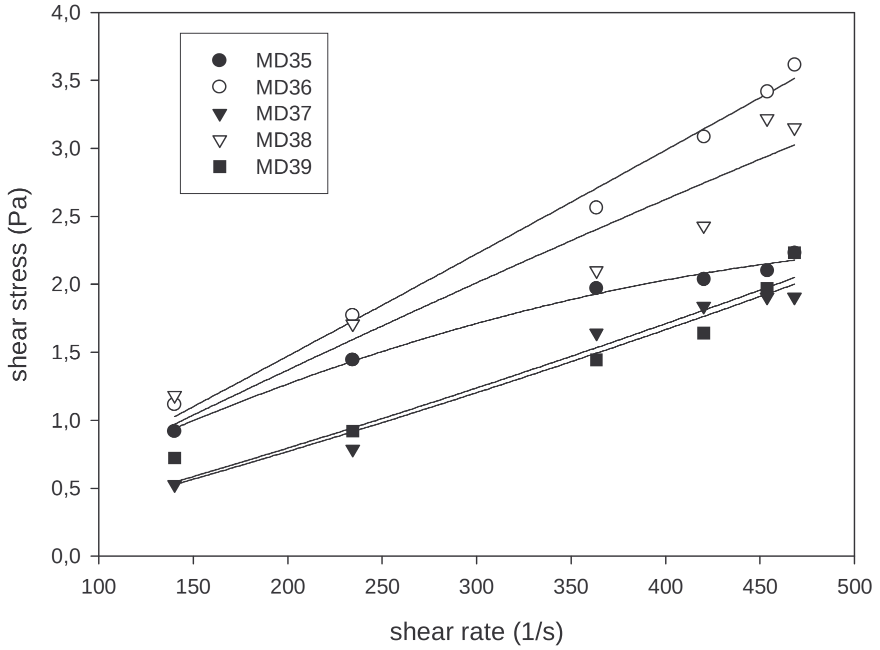

Figure 32. Rheological property of 0.5% eucalyptus methylcelluloses in DMSO solutions

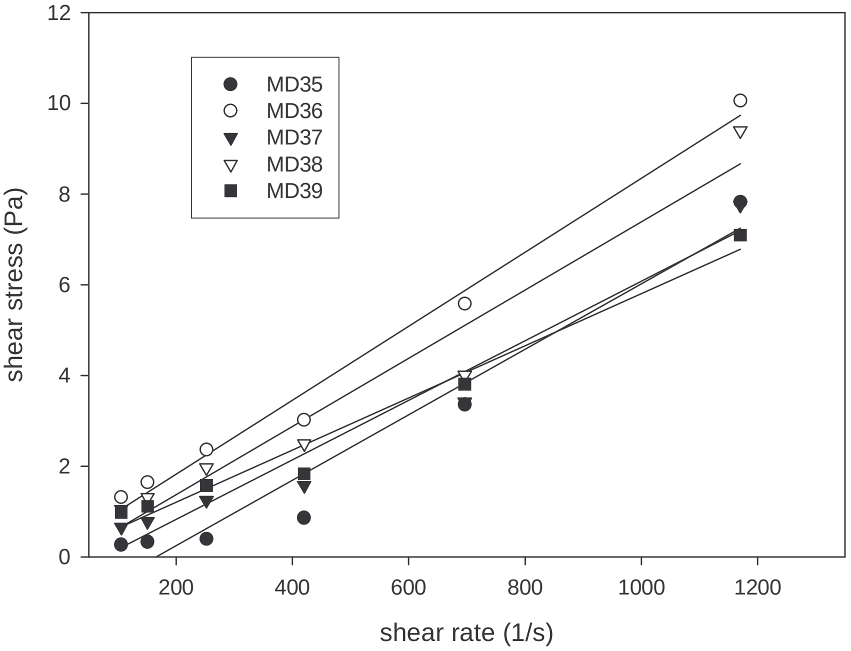

Figure 33. Rheological property of 1% eucalyptus methylcelluloses in 4% NaOH solutions

4.4. Preparation of methylcelluloses from ECF bleached pulps

4.4.1. Properties of ECF bleached pulps

Properties of ECF bleached pulps of flax, hemp, sisal, abaca and jute were determined and are listed in Table 28. Pulps used for cellulose ethers are well bleached and have high levels of purity, low lignin contents, and high α-cellulose contents (over 86 %) (Brandt, 1986). The α-cellulose contents of the flax, hemp, sisal, abaca and jute pulps in our study were higher than 87% (Table 1). Their lignin contents were lower than 0.20% (Table 1). These ECF-bleached pulps satisfied the requirements for raw materials of methylcelluloses (Brandt, 1986). Flax, hemp, sisal, abaca, and jute therefore have a new application as raw materials of methylcelluloses, thus upgrading them from low-value to high-value products.

Celluloses from annual plant plants have different chemical composition and structures (Han and Rowell, 1996; Focher et al, 2001). The most different properties of celluloses from these annual pulps are the pentosan content and the degree of polymerization (see Table 1). The flax and hemp pulps in our study had lower pentosan contents than other pulps had. The abaca pulp had the highest degree of polymerization, which indicates that the abaca pulp could be used to produce methylcelluloses of higher molecular weights. The hemp, sisal, and flax pulp could be used to produce methylcelluloses of lower molecular weights. The jute pulp was a better raw material for methylcelluloses of intermediate molecular weights.

The degree of crystallinity of each of these five pulps was more than 0.7, which meant that these pulps had more crystalline cellulose than amorphous cellulose. Amorphous cellulose has a much more accessibility and reactivity than crystalline cellulose (Timell and Purves, 1951; Krassig, 1993). The low accessibilities of these five pulps proved these pulps had less then 5.2% of accessible cellulose. Therefore, these pulps had very low reactivities. Some pretreatments were needed to improve their accessibilities and reactivities. Thus, the properties of the methylcelluloses would be improved as the results of improvements.

After hydrolysis, contents of glucose and xylose of these five pulps are listed in Table 29. The sum of the glucose and xylose content is less than the content of holocellulose in Table 28, which were due to the inhomogeneous and incomplete hydrolysis: some glucose and xylose might be further degraded or un-reacted. In Table 29, the flax pulp had the highest content of glucose and the lowest content of xylose. The sisal pulp had the lowest content of glucose and the highest content of xylose.

Table 28. Properties of ECF bleached pulps

	Flax	Hemp	Sisal	Abaca	Jute
α-cellulose (%)	89.77	88.59	88.77	89.43	87.52
Kappa number	0.82	0.55	1.33	0.78	1.21
Lignin (%)	0.12	0.08	0.20	0.12	0.18
Ash (%)	1.51	0.83	1.04	0.97	1.30
Pentosans (%)	5.32	5.22	17.68	11.67	12.59
Accessibility (mg I_2/ mg pulp)	16.59	21.24	14.88	5.38	14.51
Degree of crystallinity (%)	75	71	75	71	70
Accessible fraction* (%)	4.0	5.2	3.6	1.3	3.5
Amorphous fraction** (%)	25	29	25	29	30
Ratio of accessible and amorphous fraction (%)	16	18	14	5	12

*: Estimation by the ration of accessibility divides by 412 (the accessibility of amorphous cellulose)

**: The amorphous fraction was that 100% subtracted the degree of crystallinity.

Table 29. Glucose and xylose contents of ECF bleached pulps

	Flax	Hemp	Sisal	Abaca	Jute
Glucose (%)	86.18	86.02	70.53	80.25	76.58
Xylose (%)	5.73	5.86	8.97	7.46	8.63

4.4.2. Accessibilities and reactivities of ECF bleached pulps

4.4.2.1. Accessibilities

The accessibility of the cellulose pulp mainly depends on the amorphous cellulose because the inaccessible crystalline region has little influence (Timell and Purves, 1951; Krässig, 1993). After soda/AQ pulping, ECF bleaching and drying, pulps usually have different chemical compositions, chemical distributions of components in their pulps (Treimanis, 1996) and morphological fibrous structures, such as cellulose fibril aggregation and cellulose structure (Evans et al,. 1995; Hult et al., 2003), which strongly influence their accessibilities and reactivities (Krässig, 1993). During the pulping and bleaching of annual plants, pores (capillaries) increase due to the dissolution of solid and to swelling (Sjoström, 1981; Treimanis, 1996). The chemical reagents are known to diffuse more easily along the fibrils and reach the surface of cellulose crystals in more fibrous pulps with more porous voids. Therefore, pulps that are more fibrous have higher accessibilities and reactivities.

The accessibilities of these pulps were hemp pulp > flax pulp > sisal pulp > jute pulp > abaca pulp (Table 28). All these five pulps need to improve their accessibilities in order to increase their reactivities.

The sequence of the degree of crystallinity of these pulps, from high to low, was flax pulp = sisal pulp> hemp pulp = abaca pulp> jute pulp (see Table 28). A lower degree of crystallinity did not mean higher accessibility. For example, the abaca pulp had the lowest accessibility and a low degree of crystallinity (Table 28), which indicated that other factors as well as cellulose crystals, such as fibril aggregation (Hult et al., 2003), pores (Treimanis, 1996) and other morphological cellulose structures (Krässig, 1993), were important.

The sisal pulp had a higher degree of crystallinity than the abaca pulp but also higher accessibility (Table 28). The hemp pulp had a low degree of crystallinity but the highest accessibility (Table 28). This indicates that the species is a major factor for accessibility and reactivity.

4.4.2.2. Degrees of crystallinity

The XRD spectra of five ECF bleached pulps are showed in Figure 34. Degrees of crystallinity of five pulps are showed in Table 28. From this Table 28, the flax pulp and the hemp pulp had the similar highest value. The sisal and abaca pulps had the similar lowest value. Compare within Table 28, lower degree of crystallinity did not mean higher accessibility. For example, the abaca pulp had the lowest accessibility and degree of crystallinity. The degree of polymerization of the abaca pulp was the highest, 1928, which provided much opportunity to form the hydrogen band at both inter-molecule and intra-molecule. Therefore, the hydrogen bond strength of the abaca pulp was the strongest among these five pulps. In the amorphous region, the hydrogen bond and van der Waals forces kept the abaca cellulose tightly together and aggregated the cellulose. This aggregation leaded to collapse of capillary and voids. Therefore, the abaca pulp had little accessibility although it had higher amorphous region.

The sisal pulp and abaca pulp had almost same degrees of crystallinity while the sisal pulp had higher accessibility. This phenomenon might be caused by the hydrogen bond strength. The sisal pulp had lower degree of polymerization than the abaca pulp. Hence, the intermolecular and intramolecular hydrogen bond strength of the sisal pulp was lower than the abaca pulp. The lower hydrogen bond strength leaded to structure that is more porous and voids.

The hemp pulp had the highest degree of crystallinity and the highest accessibility. This phenomenon showed that the accessibility of pulp was mainly influenced by the amorphous region while the inaccessible crystalline region had little influence. The morphology of amorphous region was the deciding factor of accessibility. The average diameter of micro-fibrils decreased, the accessible surface of pulp increased. The disintegrated micro-fibril had more capillary and voids, and then the reagent was easier to penetrate into the cellulose. Therefore, the accessibility was bigger.

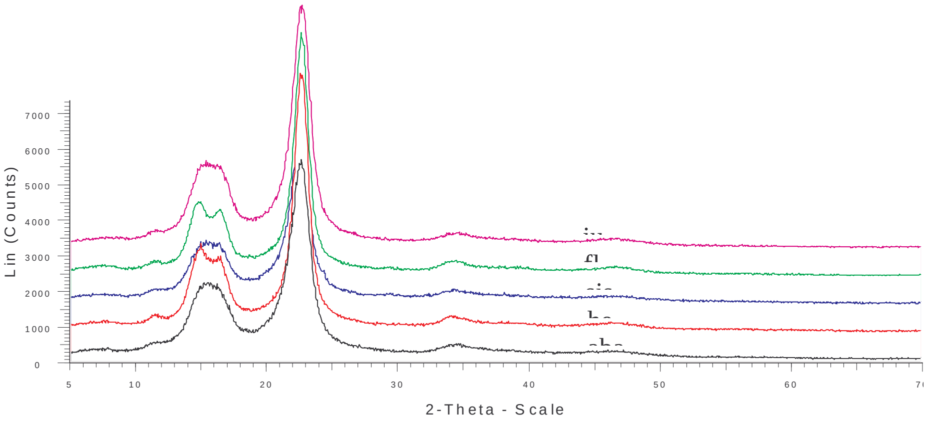

Figure 34. XRD spectra of pulps

4.4.2.3. Accessible fraction in the amorphous region

The amorphous cellulose of dried pulps is not completely accessible (Timell and Purves, 1951). Drying or irreversible hornification causes the fibrous amorphous cellulose to be partially inaccessible because some of the swollen cellulose aggregates into amorphous fibrils of a higher density, which are kept together by strong hydrogen bonds and weak van de Walls forces (Timell and Purves, 1951). These aggregated celluloses are therefore inaccessible to iodine during the determination of the accessibility of cellulose. The morphology of the amorphous cellulose is one of the main factors influencing the accessibility. Disintegration, increasing the voids and accessible surfaces of pulps, weakening the hydrogen bond strength, depolymerization, and decrystallinity are therefore essentials to improving accessibility and reactivity (Krässig, 1993). The species, however, is the deciding factor.

The sequence of the accessible fraction in the amorphous cellulose was hemp pulp> flax pulp> sisal pulp> jute pulp> abaca pulp (Table 1). The accessible fraction of the abaca pulp in the amorphous cellulose was 5% (Table 1), which indicates that about 95% of the amorphous cellulose was inaccessible. The low accessibility in amorphous cellulose is reasonable because dipole and van de Waals interactions, and intermolecular and intramolecular hydrogen bonds bind the cellulose molecules into inaccessible regions, in which hydrophobic and hydrophilic reagents cannot penetrate such well-ordered areas (Krässig, 1993). This small accessible fraction shows that most microfibrils were aggregated and few voids were available in the abaca pulp. Most of the amorphous cellulose of the other four pulps was also inaccessible. The hemp pulp had a little more accessible amorphous cellulose than the other four pulps. This hemp pulp therefore had the highest reactivity and the greatest accessibility of the five pulps.

It is essential to active these pulps in order to improve their reactivities and accessibilities before subsequent methylations. Otherwise, synthesized methylcelluloses will have partially unreacted celluloses and lower properties, such as a lower degree of substitution and a lower molecular weight of water-soluble methylcelluloses (Krässig, 1993).

4.4.2.4. Morphology by SEM

Figure 35, 36, 37, 38, and 39 are the SEM photos of these five pulps. From these figures of SEM, the inhomogeneous pulp was observed. The diameter of fibrils was heterogeneous. The void of the fibrils was randomly distributed. The aggregated microfibrils were also distributed randomly. The inhomogeneous effect will lead to the inhomogeneous methylation reaction in both the total fibrils and a single fibril. Thus, the inhomogeneous methylation will lead to poor solubilities of synthesis methylcelluloses.

From these five SEM photos, their morphological fibril structures were quite different. The hemp pulp had many small-branched thin fibrils. The flax pulp had less small-branched thin fibrils. The jute pulp had few small-branched thin fibrils. The sisal and abaca pulp did not had small-branched thin fibrils. The small-branched thin fibril had much smaller diameter. The small-branched thin fibril was distributed randomly and adhered onto the surface of other bigger fibril.

The hemp pulp fibrils had a lot of small holes and wrinkles on its surface. The hemp pulp fibrils seemed to be ruptured into smaller fibrils. The SEM photo showed the hemp pulp was well cooking during the pulping. The flax pulp fibrils had less small holes and wrinkles. Only some flax pulp fibrils seemed to be separated into smaller fibrils. The fibril surface of the jute pulp had few holes. The abaca and sisal pulps had very few holes and some wrinkles on the surface of fibrils.

These five SEM figures clearly showed the structure of small fibrils of these pulps. Base on their morphological structure, the accessibilities and reactivities can be estimated as hemp pulp> flax pulp> jute pulp> sisal pulp> abaca pulp. This sequence was same as the accessibility sequence determined by the iodine adsorption.

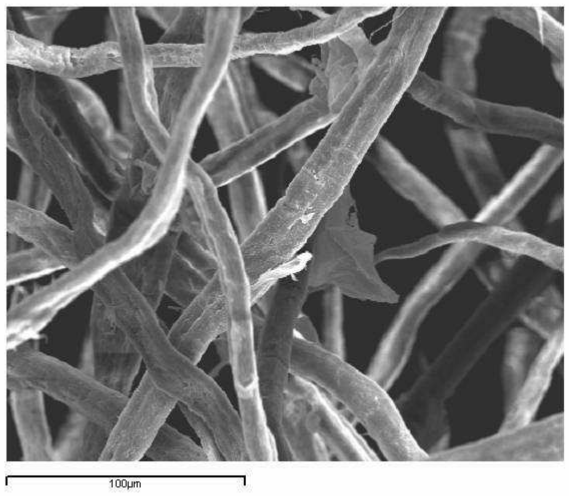

Figure 35. The morphology of abaca pulp

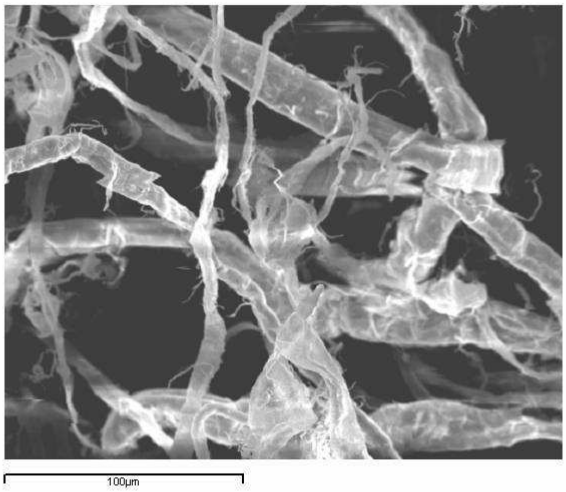

Figure 36. The morphology of flax pulp

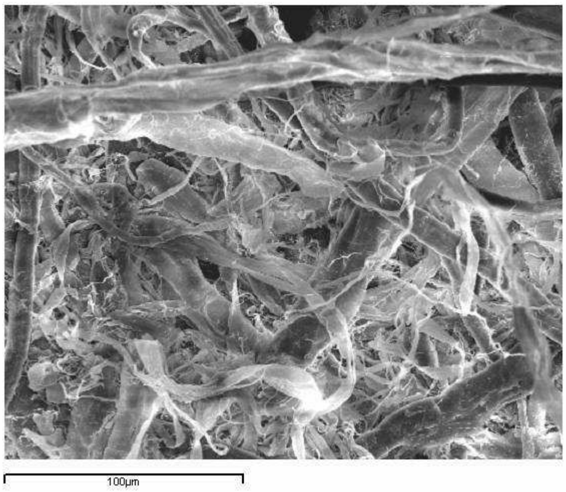

Figure 37. The morphology of hemp pulp

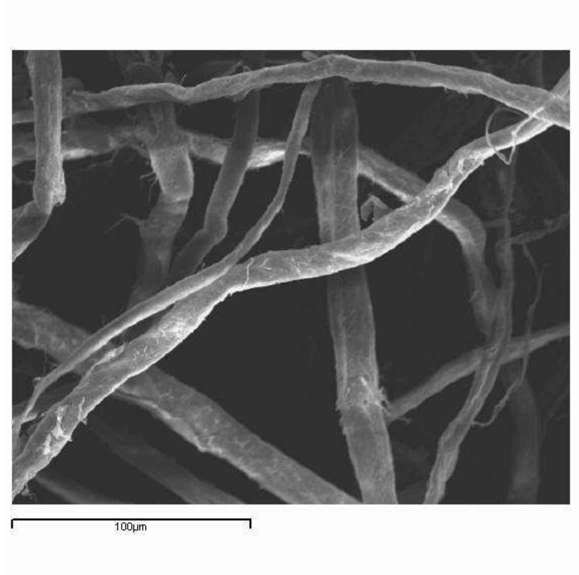

Figure 38. The morphology of jute pulp

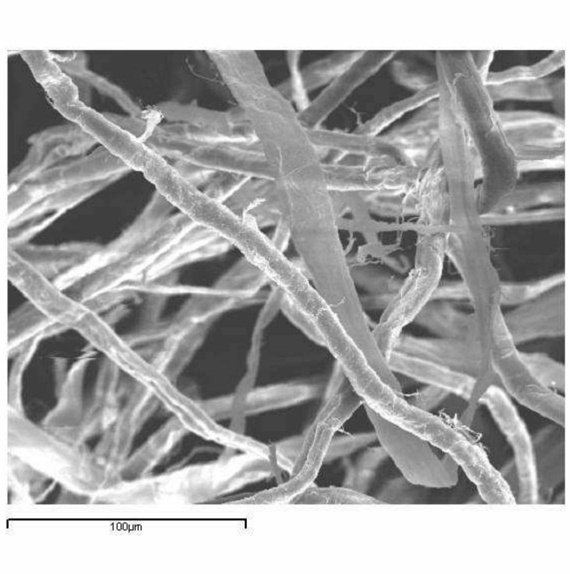

Figure 39. The morphology of sisal pulp

4.4.2.5. Effect of pretreatments

The relative crystallinity index of each pulp was significantly decreased by mercerization and preliminary mercerization (Table 30). The mean hydrogen bond strength of each pulp (Table 30), which relates to assemblies of cellulose and elementary fibrils together (Krässig, 1993), is weakened also by pretreatments (Krässig, 1993). During the mercerization and preliminary mercerization, strong swelling action and forces rupture inter-fibrils, thus increasing the accessible internal surface (Krässig, 1993). The strong swelling action and forces open intra- and inter-hydrogen bonds, thus causing the lattice transformation and the penetration of sodium hydrate ions into the widened space between the 101 lattice sheets (Krässig, 1993).

After mercerization and preliminary mercerization, the sisal and abaca pulps had a higher crystallinity index than the others (Table 30), which indicates that they were more difficult to mercerize.

Figure 40 shown the FTIR spectra of flax pulp, mercerized flax pulp and pre-mercerized flax pulp. Flax had the highest initial crystallinity index but, after mercerization, it was among the lowest of the five pulps (Table 30). Thus, flax was easily treated to improve its accessibility and reactivity by mercerization.

The abaca pulp was the most difficult to be activated in order to improve accessibility and reactivity (Table 30). All pretreatments of the abaca pulp had a positive influence on its properties. Water soaking did not change crystallinity very much but it greatly decreased the mean hydrogen bond strength (Table 30) by swelling and solvent penetration (Krässig, 1993). Mercerization under 15 bars decreased the relative crystallinity index (Table 30) and the degree of polymerization (Table 32). Steam explosion did not change the crystallinity index much either. However, it did decrease the mean hydrogen bond strength (Table 30) and the degree of polymerization (Table 32). Because both the crystallinity index and the mean hydrogen bond strength decreased, the accessibility and reactivity of the treated abaca pulps increased (Table 35).

The intrinsic viscosities of the treated pulps decreased after mercerization and after preliminary mercerization (Tables 31 and 32). Mercerization reduced the degree of polymerization and increased the accessibility and reactivity of the pulps (Table 34). Water soaking did not change the intrinsic viscosity or degree of polymerization (Table 32). Mercerization and mercerization under 15-bar pressure seemed to have a similar effect on the intrinsic viscosities (Table 32). Neutral steam explosion decreased the intrinsic viscosity of the abaca pulp (Table 32). Preliminary mercerization decreased the intrinsic viscosity considerably because the pulps were kept in an alkaline environment for a long time (Table 32).

Table 30. Properties measured by FTIR

Pulp	Treatment	Relative crystallinity index*	Mean hydrogen bond strength**
Flax	Original	5.2	11.4
Flax	Mercerization	0.3	9.3
Flax	Preliminary mercerization	0.3	10.8
Hemp	Original	5.0	10.4
Hemp	Mercerization	0.3	10.3
Hemp	Preliminary mercerization	0.2	10.0
Sisal	Original	2.6	11.4
Sisal	Mercerization	0.6	10.9
Sisal	Preliminary mercerization	0.5	10.8
Abaca	Original	2.3	11.2
Abaca	Mercerization	0.5	9.3
Abaca	Preliminary mercerization	0.5	9.4
Abaca	Water, 1h	2.2	7.3
Abaca	Pressure mercerization	0.6	9.9
Abaca	Steam explosion	1.8	9.2
Jute	Original	2.6	10.6
Jute	Mercerization	0.3	9.6
Jute	Preliminary mercerization	0.3	10.2

*: Calculated by $A_{1375}/A_{2900.}$

**: Calculated by $A_{3300}/A_{2900.}$

Table 31. Intrinsic viscosities of preliminarily treated pulps

Pulp	Flax	Hemp	Sisal	Abaca	Jute
Original intrinsic viscosity (ml/g)	747	659	640	1253	946
Mercerized intrinsic viscosity (ml/g)	707	589	626	1032	564
Preliminarily mercerized intrinsic viscosity (ml/g)	547	588	614	917	540

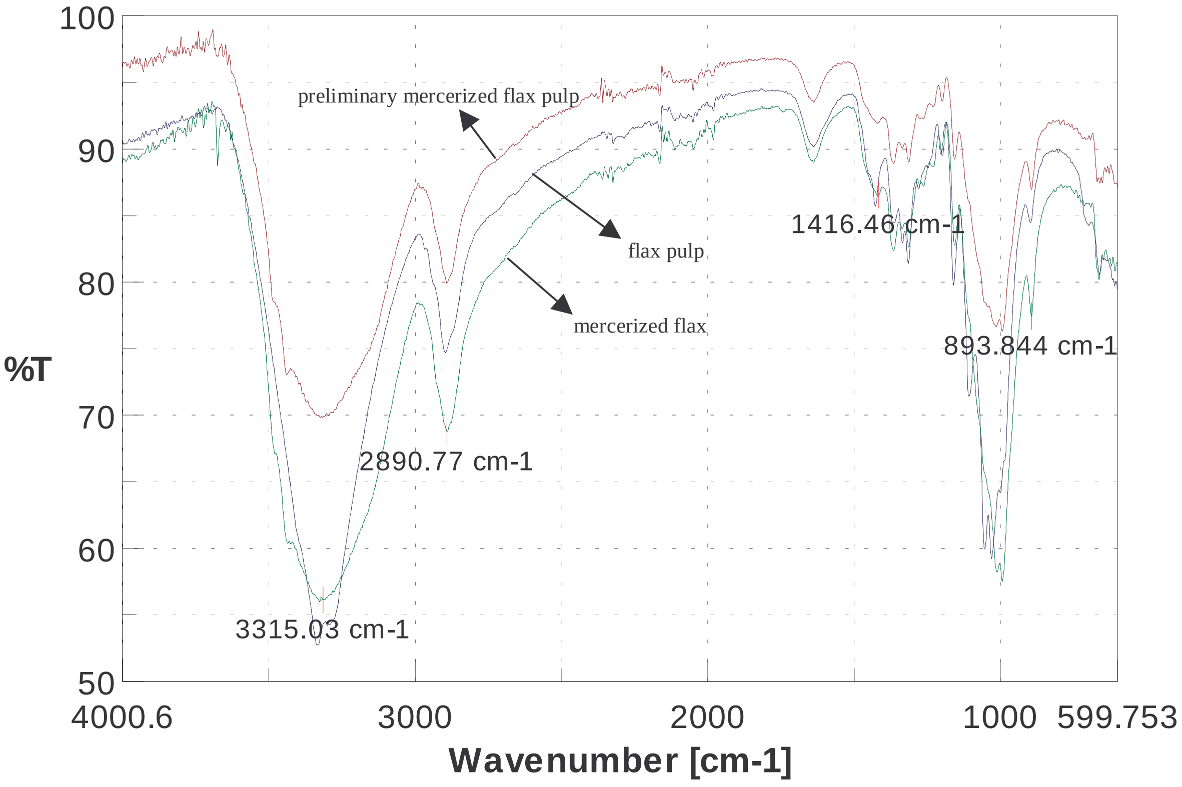

Figure 40. FTIR spectra of flax pulps

Table 32. Intrinsic viscosities of preliminarily treated abaca pulps

Pretreatments	Intrinsic viscosity (ml/g)
Original abaca pulp	1253
Water soaking	1199
Mercerization	1032
Mercerization under pressure	1004
Steam explosion	995
Preliminary mercerization	917

4.4.2.6. Reactivities of ECF bleached pulps

The unreacted pulp content was related to the accessibility and reactivity of the pulp (Tables 28 and 33). The abaca pulp had the lowest accessibility (Tables 28), so it had the highest unreacted pulp content (Table 33). The hemp pulp had the highest accessibility (Tables 28), so it had the lowest unreacted pulp content (Table 33). For the methylation of pulps without pretreatments, the unreacted pulp content was related to the inaccessibility of the pulps. In other words, the methylcellulose content was proportional to the accessibility. When pulps were not pretreated, the main component of methylcelluloses was alkali-soluble methylcellulose.

After preliminary mercerization, the unreacted pulp content decreased considerably (Table 34). The flax and abaca methylcelluloses had not un-reacted pulp (Table 34). The hemp, sisal and jute methylcelluloses had little unreacted pulp (Table 34). The water-soluble methylcellulose content increased after preliminary mercerization, while the alkali soluble methylcellulose content decreased. These data indicate that preliminary mercerization increased the reactivity of the pulps. The final effect of preliminary pretreatment depended on the characteristics of the pulps: pore content and distribution, content and distribution of lignin and hemicellulose, and fibril aggregations (Krässig, 1993). Pulps of low accessibility and low degrees of crystallinity, such as the abaca pulp, could use preliminary mercerization to improve accessibility and reactivity. However, pulps of high accessibility and high degrees of crystallinity, such as the hemp pulp, had less effect.

Several pretreatments were carried out with the abaca pulp (Table 32). Water soaking reduced the unreacted pulp content considerably (Table 35). During the one-hour of water soaking, water diffused and penetrated the capillary and voids, and the pulp swelled. Water weakened the hydrogen bond strength (Table 30) and separated the aggregate fibrils (Krässig, 1993), which was confirmed by the FTIR spectrum. Mercerization under 15 bars of pressure reduced the unreacted abaca pulp content to 0% (Table 35). The pressure of 15 bars helped the alkaline solution to penetrate the capillaries, increased the velocity of penetration, and therefore improved the swelling effect. The distribution of the alkali solution in the pulp was therefore uniform, which helped the iodomethane to diffuse and react with alkali cellulose. Steam explosion and preliminary mercerization significantly improved the water-soluble methylcellulose content (Table 35). The methylcellulose samples of the abaca pulp had a water-soluble methylcellulose content of almost 50% (MD53 and MD47, Table 35). Steam explosion could reduce the degree of polymerization by oxidation at high temperature and disintegrate the aggregated fibrils by a sudden evaporation of the liquid in the voids when the pressure is suddenly decompressed (Yamashiki et al., 1990a, b, c). The abaca pulp treated by steam explosion therefore had considerable accessibility.

Table 33. Fractionation of methylcelluloses of conventionally mercerized pulps

MC	MD45	MD41	MD44	MD55	MD42
Pulp	Flax	Hemp	Sisal	Abaca	Jute
Water-soluble methylcellulose (%)	11.03	16.67	18.82	12.50	18.48
Alkali soluble methylcellulose (%)	72.47	68.41	43.53	48.56	62.46
Un-reacted pulp (%)	16.51	14.93	37.66	38.94	19.06

Table 34. Fractionation of methylcelluloses of preliminarily mercerized pulps

MC	MD58	MD59	MD46	MD47	MD57
Pulp	Flax	Hemp	Sisal	Abaca	Jute
Water-soluble methylcellulose (%)	56.52	33.73	27.41	51.72	30.64
Alkali soluble methylcellulose (%)	43.48	62.23	64.45	48.28	66.74
Un-reacted pulp (%)	0.00	4.04	8.14	0.00	2.62

Table 35. Fractionation of methylcelluloses of preliminarily treated abaca pulps

MC	MD55	MD48	MD54	MD53	MD47
Pretreatments	Non	Water soaking	Mercerization with pressure	Steam explosion	Preliminary mercerization
Water-soluble methylcellulose (%)	12.50	18.75	14.63	49.23	51.72
Alkali soluble methylcellulose (%)	48.56	77.27	85.37	50.77	48.28
Un-reacted pulp (%)	38.94	3.98	0.00	0.00	0.00

4.4.3. Methylation of ECF bleached pulps

4.4.3.1. Methylation of non-pretreated pulps

Main properties of synthesized methylcelluloses are listed in Table 36. The appearance of bond 2830 in Figure 41 shows that the methylcellulose of the non-pretreated jute pulp was synthesized. The spectrum in Figure 41 was same as the FTIR spectra of methylcelluloses synthesized from non-pretreated flax, abaca, sisal and hemp pulps. Each synthesized methylcellulose was a mixture of water-soluble methylcellulose, alkali-soluble methylcellulose and unreacted cellulose (Table 36; Ye and Farriol, 2005b). These methylcelluloses partially dissolved in 4% NaOH, DMSO, and water (Table 36). These methylcelluloses contained different amounts of unreacted pulps. Pretreatments were therefore needed to improve the accessibilities and reactivities of these pulps (Ye and Farriol, 2005b) and thus improve the properties of these synthesized methylcelluloses.

The molecular weights and degrees of polymerization of water-soluble methylcellulose (Table 36) were lower than its original pulp (Table 28), which meant that the cellulose was degraded during the synthesis of methylation. The abaca pulp had the highest degree of polymerization (see Table 28), but the synthesized abaca methylcellulose (MD55) had the lowest (see Table 36). This was due to its lower accessibility (Ye and Farriol, 2005b), which hindered the diffusion and penetration of reagents into the interior of the fiber, where the cellulose is less degraded (Krassig, 1993). The flax pulp had a higher accessibility and a higher reactivity than the other four pulps (Ye and Farriol, 2005b). The flax methylcellulose (MD45) therefore had a higher degree of polymerization than the synthesized methylcelluloses of the other four pulps (see Table 36). These data show that not only accessibility but other factors such as the degree of polymerization and fiber morphology also influenced the properties of synthesized methylcelluloses (Ye and Farriol, 2005b).

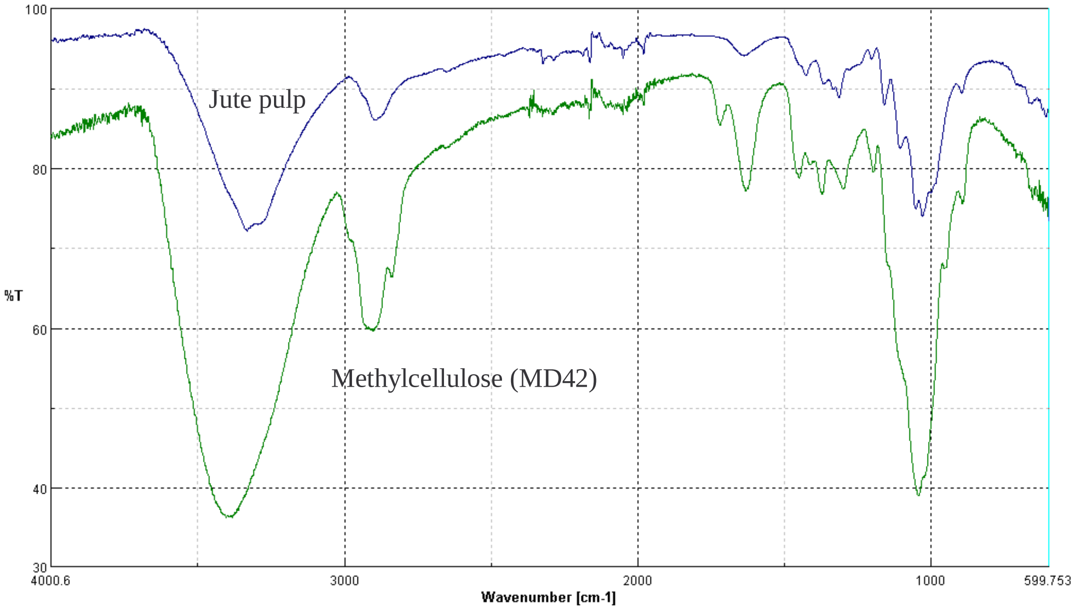

Figure 41. FTIR spectra of jute pulp and MD42 of jute

Table 36. Properties of methylcelluloses synthesized by conventional method

ECF bleached Pulp	Flax	Hemp	Sisal	Abaca	Jute
Methylcellulose	MD45	MD41	MD44	MD55	MD42
Solubility in 4% NaOH	partial	partial	partial	partial	partial
Solubility in DMSO	partial	partial	partial	partial	partial
Solubility in water	partial	partial	partial	partial	partial
DP*	1084	600	893	535	863
Molecular weight*	202880	112400	167180	100140	161640
Intrinsic viscosity**	255.5	208.9	114.3	219.7	127.7
Water-soluble content (%)	11.03	16.67	18.82	12.50	18.48
Alkali-solubel content (%)	72.47	68.41	43.53	48.56	62.46
Un-reacted pulp (%)	16.51	14.93	37.66	38.94	19.06

*: Water-soluble methylcellulose.

**: Alkali-soluble methylcellulose.

Since the main component of these synthesized methylcelluloses is alkali-soluble methylcellulose, these pulps could be used to produce alkali-soluble methylcelluloses without pretreatment. The jute pulp was degraded much more than the abaca pulp (see Tables 28 and 36). Sisal methylcellulose had the lowest intrinsic viscosity because its original pulp had the lowest degree of polymerization (see Tables 28 and 36). Flax methylcellulose had the highest intrinsic viscosity, which mean that the highest accessibility and reactivity could lead to the highest quality of methylcellulose (Krassig, 1993). These phenomena also show that the flax pulp was the best material for producing alkali-soluble methylcellulose without pretreatment.

4.4.3.2. Methylation of pre-mercerized pulps

The pulps were pre-mercerized in 15% NaOH solution for 15 minutes, pressed to a press factor of about 3, and kept in the air for 4 hours (Croon and Manley, 1963). Table 37 shows the properties of five pulps treated by preliminary mercerization. The celluloses of these five pulps were degraded and their intrinsic viscosities were lower after preliminary mercerization (see Table 37). Their accessibilities greatly improved after this preliminary mercerization (Table 37), though the abaca and hemp pulps still had lower accessibilities and lower amorphous cellulose contents (Krassig, 1993).

Table 37. Accessibilities and intrinsic viscosities of pre-mercerized celluloses

ECF bleached Pulp	Flax	Hemp	Sisal	Abaca	Jute
DP	788	847	884	1320	778
Intrinsic viscosity (ml/g)	547	588	614	917	540
Accessibility	289	253	330	262	272
Amorphous fraction (%)	70	61	80	64	66

Table 38 shows the properties of methylcelluloses synthesized from the pre-mercerized pulps. The appearance of bond 2830 in Figure 42 shows that the methylcellulose of pre-mercerized flax pulps was synthesized. The spectrum in Figure 42 was the same as the spectra of methylcelluloses of pre-mercerized jute, abaca, sisal and hemp. The solubilities of flax and abaca methylcelluloses were improved by this preliminary mercerization but the unreacted contents of methylcelluloses were decreased. The alkali-soluble contents of methylcelluloses significantly increased.

The molecular weights and degrees of polymerization of water-soluble flax, hemp and abaca methylcelluloses in Table 38 were higher than those of water-soluble methylcelluloses without pretreatment in Table 36. The intrinsic viscosities of alkali-soluble methylcelluloses of all the pulps were improved by this preliminary mercerization. These data show that the properties of methylcelluloses would improve if the accessibilities of their pulps were increased by suitable pretreatment (Ye and Farriol, 2005b).

These data show that preliminary mercerization was only suitable for the flax and abaca pulps, while other pulps needed other pretreatments. The hemp, sisal and jute methylcelluloses (MD59, MD46 and MD57, respectively) had very low water-soluble contents and high alkali-soluble contents, which means that preliminary mercerization was not suitable for the hemp, sisal or jute pulps.

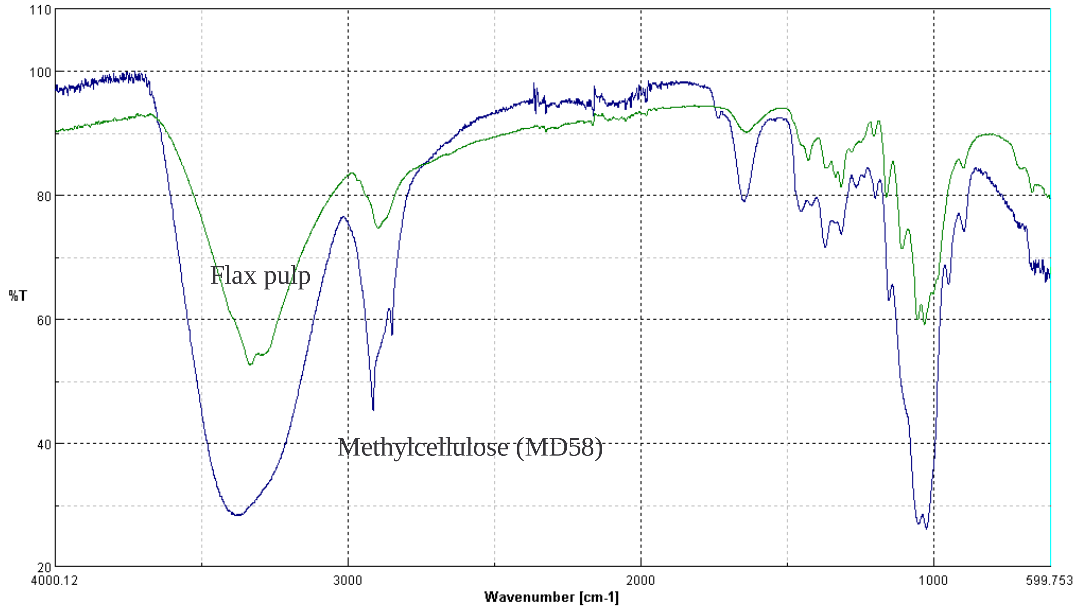

Figure 42. FTIR spectra of flax pulp and MD58 of flax

Table 38. Properties of methylcelluloses of pretreated pulps

ECF bleached Pulp	Flax	Hemp	Sisal	Abaca	Jute
Methylcellulose	MD58	MD59	MD46	MD47	MD57
Solubility in 4% naoh	complete	partial	partial	complete	partial
Solubility in DMSO	complete	partial	partial	complete	partial
Solubility in water	partial	partial	partial	partial	partial
Total DS	1.45	-	-	1.36	-
DS_2	0.65	-	-	0.63	-
DS_3	0.36	-	-	0.33	-
DS_6	0.43	-	-	0.40	-
DP*	1102	760	719	1142	770
Molecular weight*	206310	142210	134700	213890	144230
Intrinsic viscosity**	593.7	220.0	526.7	715.1	335.8
Water-soluble content (%)	56.52	3.73	7.41	51.72	0.64
Alkali-soluble content (%)	43.48	82.23	74.45	48.28	86.74
Un-reacted content (%)	0.00	14.04	18.14	0.00	12.62

*: Water-soluble methylcellulose.

**: Alkali-soluble methylcellulose.

The solution properties of the methylcelluloses (MD46, MD57, MD58, and MD59) in dilute 4% NaOH solutions are shown in Figures 43. All these curves seemed to increase linearly i.e. shear stress values increased as shear rate values increased. All these methylcellulose solutions were Newtonian. The curves were similar although their methylcelluloses had different viscosities and substituted patterns. The rheological properties of these methylcelluloses were similar to those of other annual plant methylcelluloses (Ye et al., 2005a, b).

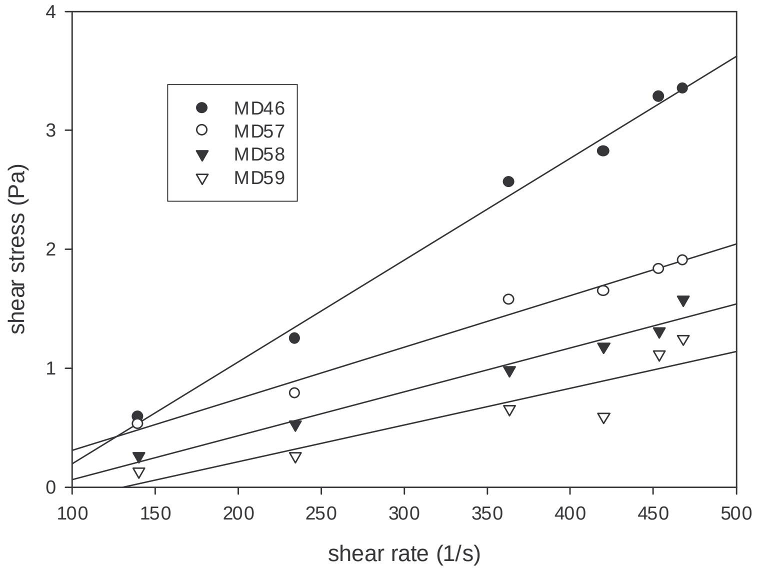

Figure 43. Rheological property of 0.5% methylcelluloses in 4% NaOH solution

The degree of substitution of the flax methylcellulose (MD58; Table 38) was higher than that of the abaca methylcellulose (MD47; Table 38). MD58 and MD47 had similar molecular weights to those of water-soluble methylcelluloses (see Table 38). The intrinsic viscosity of alkali-soluble methylcellulose of MD47 was higher than that of MD58 (see Table 38).

4.4.3.3. Abaca methylcelluloses

The properties of celluloses after pretreatments are listed in Table 39. After these pretreatments, their degrees of polymerization decreased (except water soak) and their accessibilities increased (Table 39). Pulps treated by preliminary mercerization had the lowest degree of polymerization, which meant that their cellulose was degraded more than other pulps treated by other pretreatments (Table 39) and their accessibility and amorphous contents were therefore the highest of all treated pulps (Table 39). Impregnation under 15 bars and steam explosion had similar functions to the degree of polymerization, while the pulp treated with 15 bars had 50% more accessibility and amorphous content (Table 39). Water soaking had the least influence on accessibility or amorphous content (Table 39).

Table 39. Properties of pretreated abaca pulps

	Non-pretreatment	Water soak	Preliminary mercerization	Impregnation under 15 bars	Steam explosion
DP	1918	1886	1404	1537	1523
Intrinsic viscosity (ml/g)	1253	1232	917	1004	995
Accessibility	5.38	103.53	262.28	243.88	162.37
Amorphous fraction (%)	1.31	25.13	63.66	59.19	39.41

Bond 2830 in Figure 44 shows that the methylcellulose of pretreated abaca pulps was synthesized. The spectrum in Figure 44 was the same as the spectra for methylcelluloses of abaca pulps pretreated by other methods. Figure 45 shows a NMR spectrum of abaca miscanthus (MD47), in which the methylated hydroxyl groups were shown. The properties of abaca methylcelluloses are shown in Table 40. These four pretreatments significantly increased the solubilities of methylcelluloses in 4% NaOH solution and DMSO. The degrees of polymerization and molecular weights of water-soluble abaca methylcelluloses were also improved by these pretreatments. The intrinsic viscosities of alkali-soluble abaca methylcelluloses also improved. After these pretreatments, the unreacted contents of synthesized methylcelluloses significantly decreased. The methylcellulose treated by water soaking had a very low unreacted content, while those of abaca pulps treated by the other three pretreatments had almost no unreacted contents.

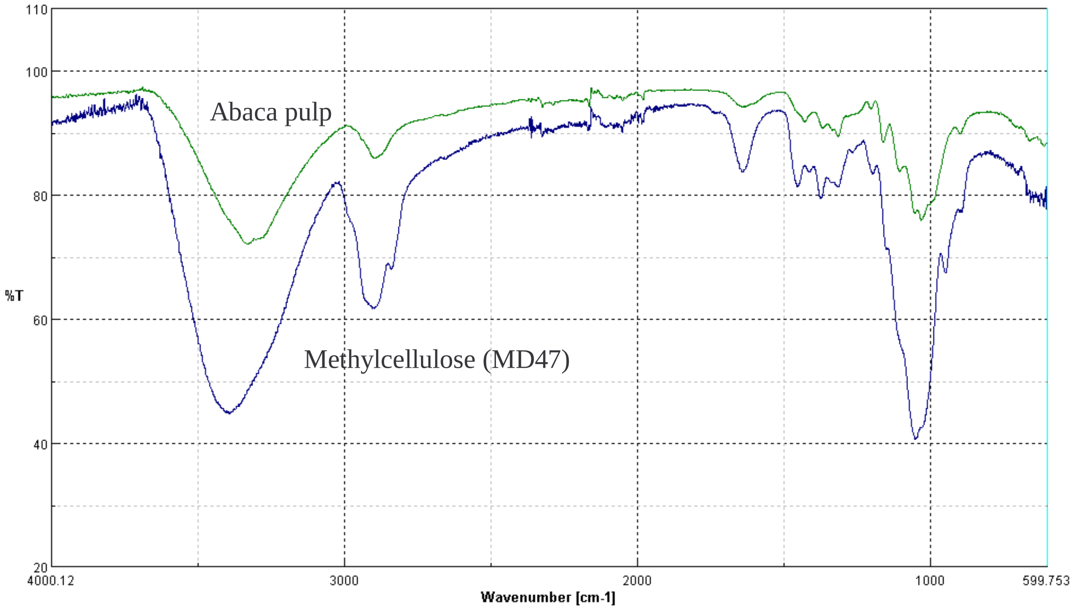

Figure 44. FTIR spectra of abaca pulp and MD47 synthesized after preliminary mercerization

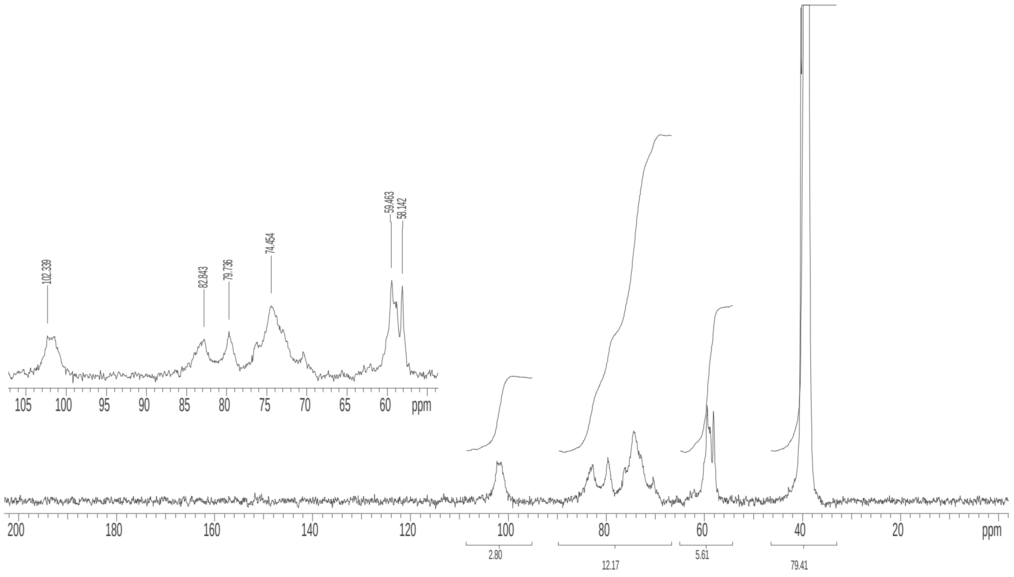

Figure 45. ^{13}C NMR spectrum of MD47 synthesized after preliminary mercerization

Table 40. Properties of methylcelluloses prepared from abaca pulps

	Non-pretreatment	Water soak	Preliminary mercerization	Impregnation under 15 bars	Steam explosion
Methylcellulose	MD55	MD48	MD47	MD54	MD53
Solubility in 4% NaOH	partial	partial	complete	complete	complete
Solubility in DMSO	partial	partial	complete	complete	complete
Solubility in water	partial	partial	partial	partial	partial
DS	0.42	0.72	1.36	0.80	1.02
DS_2	0.19	0.33	0.63	0.37	0.40
DS_3	0.08	0.17	0.33	0.18	0.30
DS_6	0.15	0.22	0.40	0.25	0.32
DP*	535	745	1142	728	1303
Molecular weight*	100140	139560	213890	136380	243950
Intrinsic viscosity	219.7	497.2	715.1	385.8	481.8
Water-soluble content (%)	12.50	18.75	51.72	14.63	49.23
Alkali-soluble content (%)	48.56	77.27	48.28	85.37	50.77
Un-reacted pulp (%)	38.94	3.98	0.00	0.00	0.00

*: Water-soluble methylcellulose.

**: Alkali-soluble methylcellulose.

Completely soluble DMSO methylcelluloses were synthesized from abaca pulps pretreated by preliminary mercerization, impregnation under 15 bars, and steam explosion. The abaca methylcellulose synthesized from the steam-exploded abaca pulp had the highest degree of polymerization and highest molecular weight of all abaca methylcelluloses. Water-soaking and mercerization under 15 bars had similar functions to the synthesized abaca methylcelluloses, which had similar degrees of substitution, degrees of polymerization, and molecular weights. However, the intrinsic viscosity of alkali-soluble methylcellulose synthesized from water-soaked pulp was much higher than that of methylcellulose synthesized from mercerized pulp under 15 bars. The differences in intrinsic viscosities were due to the alkali reaction of mercerization, which is known to degrade the cellulose molecules (Croon and Manley, 1963; Krässig, 1993).

The degrees of substitution were significantly improved by preliminary mercerization and steam explosion (see Table 40). The abaca methylcellulose synthesized (MD53) from steam-exploded pulp had a lower degree of substitution but a higher molecular weight and a higher degree of polymerization than the abaca methylcellulose (MD47) synthesized from preliminary mercerized pulp. The alkali-soluble methylcellulose of MD47 had a much higher intrinsic viscosity than that of MD53. For the synthesis of water-soluble methylcellulose with a high molecular weight, the best pretreatment was steam explosion.

4.4.3.4. Homogeneous methylation

Bond 2830 in Figure 46 shows that the methylcellulose of abaca pulp was synthesized by homogeneous methylation. The spectrum of MD51 had a stronger methoxyl bond peak than the spectrum of MD47, which shows that MD51 had a higher degree of substitution than MD47. The properties of abaca methylcellulose synthesized by homogeneous methylation are listed in Table 41. The starting methylcellulose was MD47. The synthesized methylcellulose (MD51) was completely soluble in cold water. Homogeneous methylation increased its solubility in cold water. The degree of polymerization, molecular weight, and intrinsic viscosity of MD51 were lower than MD47, which meant the cellulose chain was degraded during the homogeneous methylation. The degree of substitution of MD51 was close to that of commercial methylcellulose (Brandt, 1986). Also, as it had an intermediate molecular weight, it can be used as an additive in the construction industry and in the manufacture of paints, medicines and polymerization products, etc.

Table 41. Properties of methylcellulose of homogeneous methylation

Methylcellulose	MD51
Solubility in water	Complete
Solubility in DMSO	Complete
Total DS	1.72
DS_2	0.75
DS_3	0.44
DS_6	0.53
DP*	591
Molecular weight*	110600
Intrinsic viscosity (ml/g)*	652.3
Water-soluble content (%)	100%

*: Measured in water.

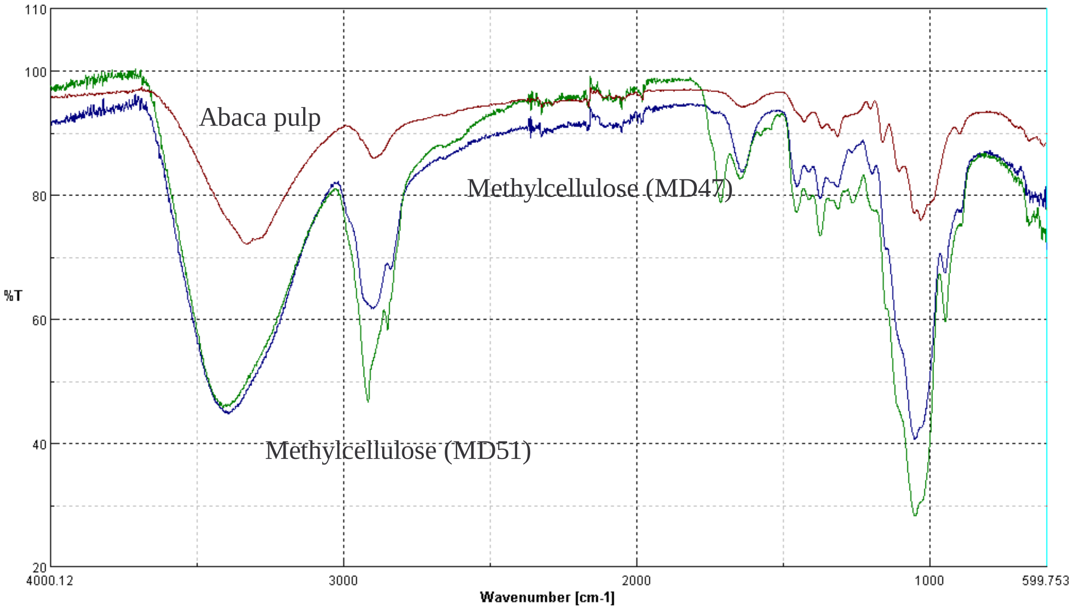

Figure 46. FTIR spectra of abaca pulp, MD47 and MD51

4.5. Factors influencing the molecular weight

4.5.1. Effect of the pulping condition

Chemical pulping is a very important step in the production of dissolving pulps for cellulose derivatization (Fengel and Wegener, 1984). The pulping eliminates most of the lignins and some of the hemicellulose, which will reduce most impurities and increase the voids in the cellulose (Fengel and Wegener, 1984; Ye and Farriol, 2005b). The chemical pulping further breaks up the aggregated fibrils and microfibrils, which increases the accessible surface for reagents to react with the cellulose (Fengel and Wegener, 1984; Ye and Farriol, 2005b). The present pulping process consisted of impregnation and steam pulping (or steam cooking).

4.5.1.1. Effect of the impregnation condition

The main impregnation parameters of spring cardoon are listed in Table 42. All the experiments on spring cardoon were carried out at the same pulping severity (2.96). The molecular weights of water-soluble methylcelluloses are listed in Table 43. MD27 and MD30 stalks had the same impregnation retention time while the MD27 stalk was impregnated at a lower concentration of NaOH solution. The MD30 had a lower Mw and DP than MD27. A higher concentration of the impregnation NaOH solution led to a lower molecular weight of the methylcelluloses synthesized because the 30% NaOH solution degraded the cellulose more than the 20% NaOH solution during the impregnation (Krassig, 1993).

Table 42. Main impregnation parameters of spring cardoon samples

MC	NaOH (%)	Time (Hour)
MD27	20	2
MD28	30	1
MD20	30	1.5
MD30	30	2

Table 43. Molecular weights of water-soluble methylcelluloses prepared from spring cardoon

MC	Plant	Mn[a]	Mw[b]	Pd[c]	DP[d]
MD28	Spring cardoon	8021	54543	6.8	291
MD20	Spring cardoon	25980	140880	5.4	752
MD30	Spring cardoon	40174	175360	4.4	937
MD27	Spring cardoon	34471	218340	6.3	1166

[a]Number average molecular weight; [b]weight average molecular weight; [c]polydispersity; [d]degree of polymerization.

The MD28, MD20, and MD30 stalks were impregnated at the same concentration of NaOH solution but at increasing impregnation times. When the impregnation time was longer, the methylcellulose properties were better. Their Mw and DP increased at longer impregnation retention times. This phenomenon can be explained by the impregnation mechanism and methylation reaction (Ye and Farriol, 2005a). When the stalk was impregnated for a longer time, more NaOH solution diffused and penetrated into the inner capillaries and voids of the stalks, which was vital for the fibrillation and delignification of pulping (Ye and Farriol, 2005a). After the pulping and bleaching, the accessibility of the pulp was better. In addition, more lignin was removed; more voids and capillaries were created; more aggregated micro-fibrils were separated. Thus, the reactivity of the pulp was better, which favored and facilitated the diffusion of the methylation reagent and NaOH solution in the bleached pulp. The methylation of the bleached pulp was a typical topochemical reaction (Timell and Purves, 1951; Rebenfeld, 1954) with the hindrance of not only residual lignins and hemicelluloses, but also the special physical morphology structures of bleached pulps. At the beginning of the methylation, the chemicals rapidly diffuse and penetrate into the accessible amorphous region and the exterior part of the fibrils. The lignin and hemicellulose, un-cooked fibrils, and aggregated microfibrils restrict the comparatively slow diffusion and penetration of reagents into the inner part of the fibrils where further methylation can proceed. Therefore, the surface of the fibers was converted, and the amorphous cellulose of the fiber was methylated. In the concentrated NaOH solution in the topochemical methylation, the cellulose of the surface and the amorphous region were degraded much more than cellulose of the inner portion of fiber. Therefore, the molecular weight was low, when the impregnation time was short. This meant that the impregnation effect was worse and that the molecular weights of synthesized methylcelluloses were low (Krassig, 1993).

The impregnation conditions for the summer cardoon stalks were different from those of spring cardoon (see Table 44). The molecular weights of methylcelluloses are listed in Table 45. The molecular weights of the summer cardoon methylcelluloses were similar. When the impregnation solution was 30% NaOH, the MD33 and MD34 had almost the same molecular weights. This indicated that the temperature had little influence on the molecular weight when the stalk was impregnated in the 30% NaOH solution. When the impregnation solution was 20% NaOH, the molecular weight of the MD31 sample was higher than that of the MD32 sample, indicating that the temperature had some influence on the molecular weight when the stalk was impregnated in the 20% NaOH solution. Based on these data, the alkaline concentration and the temperature of impregnation had very little influence on the molecular weights of methylcelluloses prepared from summer cardoon stalks.

Table 44. Impregnation conditions of summer cardoon samples

MC	NaOH (%)	Time (Hour)	Temperature (^{0}C)
MD31	20	1	Room temperature (20^{0}C)
MD32	20	1	60
MD33	30	1	Room temperature (20^{0}C)
MD34	30	1	60

Table 45. Molecular weights of water-soluble methylcelluloses prepared from summer cardoon

MC	Mn	Mw	Pd	DP
MD32	27731	146890	5.3	785
MD34	29432	156590	5.3	836
MD33	29967	158550	5.3	847
MD31	35059	168020	4.8	897

4.5.1.2. Effect of the cooking time

The cooking conditions of the miscanthus stalks are listed in Table 46. The molecular weights of water-soluble miscanthus methylcelluloses are listed in Table 47. Their cooking times greatly influenced the molecular weights of the methylcelluloses obtained. Shorter cooking times led to pulps with higher lignin and hemicellulose contents. The shorter cooking times degraded the cellulose less (Ye and Farriol, 2005a) and produced fewer voids and capillaries. What is more, the micro-fibrils of pulps with shorter cooking times aggregated much more than those of the pulps with longer cooking times. Therefore, pulps with low accessibilities and reactivities were produced using shorter cooking times. Because of the topochemical methylation mechanism (Timell and Purves, 1951; Rebenfeld, 1954), the methylation was hindered by the shorter cooking time. On the other hand, when the cooking time was longer, the surfaces, voids, and capillaries of the pulps were much more accessible. In addition, the methylation regents had more opportunity to diffuse and penetrate into the inner part of the fibers and react with the alkali cellulose. Therefore, the molecular weights of methylcelluloses were higher when the cooking times were longer. However, too long a cooking time degraded the cellulose during the cooking (Kokta and Ahmed, 1998). Therefore, an optimum cooking time needed to be tested.

Table 46. Cooking conditions of miscanthus samples

MC	Cooking time (minutes)	Temperature (^{0} C)
MD25	4	180
MD22	8	180
MD24	15	180
MD19	26	180
MD26	26*	180

*: higher volume of iodomethane in methylation

Table 47. Molecular weights of water-soluble methylcelluloses prepared from miscanthus

MC	Mn	Mw	Pd	DP
MD25	7888	20685	2.6	110
MD22	12482	99063	7.9	529
MD19	44072	190330	4.3	1017
MD24	33524	205960	6.1	1100
MD26	55050	222470	4.0	1188

When the cooking temperature was the same and the cooking time increased from 4 to 26 minutes, the water-soluble molecular weights of miscanthus methylcelluloses increased from 20,685 to 222,470. The MD25 sample, which was cooked for only 4 minutes, had a very low molecular weight and degree of polymerization. The MD24 and MD19 samples, which were cooked for 15 and 26 minutes, respectively, had similar molecular weights and degrees of polymerization. The MD26 sample was particularly interesting. It was synthesized with a greater amount of methylation reagent than the MD19 sample, although the two samples had the same cooking time, which indicated that the methylation condition had some influence on the molecular weight of water-soluble methylcelluloses.

The molecular weights of miscanthus methylcelluloses increased as the cooking time increased. Therefore, if the molecular weight of methylcelluloses was to be higher, the pulping severity also had to be higher. Since the MD26 sample had a degree of polymerization of 1188, the cooking and methylation conditions of MD26 might be optimum for the miscanthus stalks.

4.5.1.3. Effect of the cooking temperature

The cooking conditions for the eucalyptus chips are listed in Table 48. The molecular weights of eucalyptus methylcelluloses are listed in Table 49. Although the cooking conditions for the eucalyptus chips were quite different, the molecular weights of the water-soluble methylcelluloses in four samples (MD35, MD36, MD37 and MD38) were almost the same.

Table 48. Steam-pulping conditions of eucalyptus samples

MC	Reaction time (min)	Temperature (^{0}C)
MD36	8	180
MD35	16	180
MD37	24	180
MD38	16	190
MD39	24	190

Table 49. Molecular weights of water-soluble methylcelluloses prepared from eucalyptus

MC	Mn	Mw	Pd	DP
MD39	17570	104790	6.0	560
MD35	23591	127270	5.4	680
MD37	19778	133830	6.8	715
MD38	25967	147160	5.7	786
MD36	27592	160010	5.8	855

The cooking times were the same for MD37 and MD39 pulps. The MD39 pulp was cooked at a higher temperature than the MD37 pulp. The MD39 had a lower molecular weight than that of the MD37, which indicated that it had degraded much more than that of MD37 at a higher cooking temperature.

When the cooking time was the same for the MD35 and MD38 pulps, the MD38 sample was cooked at a higher temperature than MD35. The MD35 had a lower molecular weight than MD38 because of the topochemical methylation mechanism (Timell and Purves, 1951). Eucalyptus is a hardwood and its pulping severity is usually higher than that of annual plants. A low cooking temperature or pulping severity led to a low accessibility and reactivity of the pulps. Therefore, the low accessibility and reactivity of the MD35 pulp restricted the synthesis of methylcellulose to having a higher molecular weight.

When the cooking temperature was 190^0C, MD38 had a higher molecular weight than MD39. This indicated that a longer cooking time led to a higher degradation. When the cooking temperature was 180^0C, MD36 had a higher molecular weight than MD35 and MD37, which both had similar molecular weights even though the MD35 and MD37 pulps were cooked for 16 and 24 minutes, respectively. The cooking condition of MD36 may be the optimum and synthesized methylcellulose with a higher molecular weight than other cooking conditions.

4.5.2. Effect of the pretreatments

The effects of the abaca pulp pretreatments were compared. The molecular weights of water-soluble abaca methylcelluloses are listed in Table 50. When the abaca pulp was not pretreated, its molecular weight and degree of polymerization were the lowest, and its polydispersity was the highest of the five methylcelluloses. Mercerization under pressure and the water soaking method improved and increased the molecular weights and degrees of polymerization. What is more, these two methods also reduced the polydispersity. The preliminary mercerization degraded the abaca pulp and improved its accessibility and reactivity (Ye and Farriol, 2005b). The effect of the preliminary mercerization was better than that of mercerization under pressure and water soaking. The steam explosion method was the best of these four preliminary treatment methods. It increased the molecular weight and degree of polymerization 144% more than the non-preliminary treatment method.

Table 50. Molecular weights of methylcelluloses prepared from the abaca pulp

MC	Material	Pretreatments	Mn	Mw	Pd	DP
MD55	Abaca	Non	16753	100140	6.0	535
MD54	Abaca	Mercerization under pressure	28087	136380	4.9	728
MD48	Abaca	Water soaking	30132	139560	4.6	745
MD47	Abaca	Preliminary mercerization	52776	213890	4.1	1142
MD53	Abaca	Steam explosion	79373	243950	3.1	1303

Why did the molecular weights increase after different pretreatments? The pretreatments did not increase the molecular weights of cellulose; on the contrary, they usually degraded it. For example, mercerization under pressure degraded the cellulose molecule and increased the uniform distribution of NaOH solution in the voids and capillaries of the abaca pulp (Krassig, 1993). The preliminary mercerization and the steam explosion also had similar degradation functions. The pretreatments improved the molecular weight of water-soluble methylcelluloses because they increased the accessibility and reactivity of the abaca pulp. When the accessibilities and reactivities of pulps improved, the synthesized methylcelluloses had much better properties (including higher molecular weights) (Krassig, 1993).

The molecular weights of water-soluble methylcelluloses might be explained by the topochemical methylation mechanism of bleached pulp (Timell and Purves, 1951). Firstly, the methylation reaction concentrated on the accessible region of the fiber, where the molecular weight of cellulose was degraded to be lower than that of the interior of fibers and cellulose crystals. The methylation reagent cannot diffuse, penetrate, or reach the interior to react because of the lower accessibility (Krassig, 1993). Therefore, the methylation was limited to the surface and outside of the fibers and the synthesized methylcelluloses had a lower molecular weight without any pretreatments. Even the simplest water soaking had a great effect on the molecular weight of synthesized methylcellulose.

4.5.3. Effect of the methylation conditions

•-Cellulose can be considered to have no lignin or hemicellulose adhered to the surface of elementary fibrils. Bleached pulp is usually impure cellulose, with a certain amount of hemicellulose and lignin adhered to the surface of elementary fibrils (Osulliva, 1997). Hemicellulose is an amorphous polysaccharide with a low degree of polymerization, but higher accessibility, and higher reactivity than the cellulose (Fengel, 1971). Hemicellulose and the coexisting lignin competed with the cellulose to be mercerized and methylated. The aggregated fibrils hindered the diffusion of chemical reagents on the surface of interior cellulose fibrils. Therefore, the bleached pulp had less accessibility and reactivity than the •-cellulose.

The molecular weights of water-soluble methylcelluloses prepared from the α-cellulose (see Table 51) were controlled by the mechanism and kinetics of the methylation. Because the synthesis of the MD17 sample used the lowest amount of chemical methylation reagent, the molecular weight of the MD17 sample was the lowest among these synthesized methylcelluloses. The methylation concentrates on the accessible surface of fibrils (Timell and Purves, 1951). The surface cellulose of fibrils had more opportunity to react and to degrade in a concentrated NaOH solution. Therefore, the molecular weight of its methylcellulose was the lowest and the polydispersity was the highest. When the mole ratio of iodomethane and anhydroglucose was higher and same quantity of alkali charge was used in the methylation, the iodomethane had more opportunity to diffuse and penetrate into the interior of fibrils. The alkaline solution has difficulty in diffusing and penetrating into the interior of fibrils. In addition, the celluloses in interior fibrils usually have higher molecular weights. When the iodomethane reacts with the celluloses that have higher molecular weights, the synthesized methylcelluloses also have higher molecular weights. Therefore, water-soluble methylcelluloses of higher molecular weights and higher degrees of polymerization were synthesized because of more methylation reagents.

Table 51. Molecular weights of water-soluble methylcelluloses prepared from *α*-cellulose

MC	Material	CH_3I/AHG[a]	Mn	Mw	Pd	DP
MD17	α-cellulose	4.51	14339	102170	7.1	546
MD21	α-cellulose	18.06	30422	159620	5.2	853
MD23	α-cellulose	22.57	28585	181540	6.4	970
MD18	α-cellulose	13.54	34070	199500	5.9	1066
MD15	α-cellulose	9.03	42884	220340	5.1	1177

[a] Mole ratio of iodomethane and AHG (AHG stands for anhydroglucose).

The MD15 had the highest molecular weight. The degree of substitution and water-soluble methylcellulose content of MD15 were lower than those of MD18, MD21, and MD23. This indicates that the reagent ratio of the MD15 was optimum for the molecular weight, but should be higher to improve the yield of water-soluble methylcellulose and the degree of substitution.

4.5.4. Effect of the harvest time of cardoon

Two different cardoon harvests were compared: spring and summer. The molecular weights are listed in Table 43 and 45. We used only the dry stalk from the summer harvest but the total biomass from the spring harvest, including the stalk, leaves and capitula. Therefore, the spring cardoon pulp had more impure components than the summer cardoon pulp. The pulping severity of the summer cardoon, which was cooked at 170^{0}C for 4 minutes, was lower than that of the spring cardoon, which was cooked at 180^{0}C for 4 minutes.

Because of the impure components and low pulping severity, the methylation of the spring cardoon pulp was greatly influenced by the impregnation conditions. The methylation of the summer cardoon pulp, on the other hand, was influenced very little by the impregnation conditions. Thus, the leaves and capitula of spring cardoon must be removed before the pulping so that the quality of pulp for synthesizing methylcelluloses can be improved.

Although the spring cardoon was cooked at a higher pulping severity, the methylcelluloses synthesized from its pulp had much higher molecular weights than those synthesized from summer cardoon pulp. This indicated that the pulping severity of the summer cardoon needed to be increased in order to improve the molecular weights of the synthesized methylcelluloses. A higher pulping severity of the summer cardoon improved the accessibility and reactivity of the pulp (Ye and Farriol, 2005a, b). Therefore, the molecular weights of the methylcelluloses were also higher.

4.5.5. Effect of the species

4.5.5.1. Effect of the species on the Mw

Five ECF bleached pulp methylcelluloses of different molecular weights (see table 52) were synthesized under the same methylation reaction conditions.

Table 52. Methylcelluloses prepared from annual plants without pretreatments

MC	Material	DP of pulp	Mn	Mw	Pd	DP
MD55	Abaca	1928	16753	100140	6.0	535
MD41	Hemp	948	17438	112400	6.4	600
MD42	Jute	1413	23906	161640	6.8	863
MD44	Sisal	998	14171	167180	11.8	893
MD45	Flax	1165	40584	202880	5.0	1084

The abaca pulp had the highest original degree of polymerization and the lowest molecular weight of water-soluble methylcellulose. This means that the accessibility and reactivity of the abaca pulp were lower than those of other pulps (Ye and Farriol, 2005b). The degrees of polymerization of hemp and abaca methylcelluloses were similar as were those of jute and sisal methylcelluloses. The flax methylcellulose had the highest molecular weight and the lowest polydispersity. These data show that the reactivities and accessibilities of flax and sisal pulp were the highest of the five pulps (Ye and Farriol, 2005b). The abaca pulp needed to be activated in order to improve the molecular weight of the synthesized methylcelluloses. The jute and hemp pulps also had low accessibilities and reactivities. The methylcellulose of sisal pulp had a polydispersity of 11.8, which might mean that one part of the pulp was highly degraded while another part was only slightly degraded. The flax pulp was the best material for producing higher molecular weight methylcellulose without pretreatment.

4.5.5.2. Effect of the species on the pretreatments

Table 53 shows the molecular weights of the methylcelluloses prepared from five pulps that had been treated by preliminary mercerization, an effective method for improving the accessibility and reactivity of the abaca pulp. After this preliminary treatment, the molecular weights of abaca methylcellulose (MD47) and hemp methylcellulose (MD59) were higher, which demonstrated that higher accessibility and reactivity could help to increase the molecular weight of synthesized methylcelluloses. The degree of polymerization of the flax methylcellulose (MD52) was similar to that of MD45, which was synthesized from flax pulp without preliminary mercerization. The sisal methylcellulose (MD46) and jute methylcellulose (MD57) had lower molecular weights than sisal and jute methylcelluloses synthesized by the conventional mercerization method without pretreatment. This indicated that preliminary mercerization could not be used with sisal or jute pulps to improve the molecular weights. Less severe pretreatments, such as water soaking and steam explosion, can be used to improve their accessibilities and reactivities (Ye and Farriol, 2005b). The abaca and hemp pulps needed preliminary mercerization to improve the accessibilities and reactivities, which in turn improved the molecular weights of the methylcelluloses obtained. The flax pulp did not need preliminary mercerization because its accessibility and reactivity were sufficient for it to be methylated (Ye and Farriol, 2005b). After the preliminary treatment, the polydispersity of the hemp and jute methylcelluloses increased considerably, which showed that some of their pulp was considerably degraded while another portion was only slightly degraded during the synthesis.

Table 53. Methylcelluloses prepared from preliminarily mercerized pulps

MC	Material	DP of pulp	Mn	Mw	Pd	DP
MD46	Sisal	998	16642	134700	8.1	719
MD59	Hemp	948	6075	142210	23.4	760
MD57	Jute	1413	98077	144230	14.7	770
MD52	Flax	1165	32469	206310	6.4	1102
MD47	Abaca	1928	52776	213890	4.1	1142

4.6. Factors influencing the degree of substitution

4.6.1. Effect of pulping conditions

The soda pulping process is usually used to produce unbleached pulps from annual plants (Patt, 1986). The unbleached pulps are further bleached by an environmental friend bleaching process to produce cellulosic products, such as paper, paperboard, and cellulose derivatives (Ye and Farriol, 2005a). In the soda pulping process, the pulping time and temperature as well as the alkali charge are the main parameters, which influence the contents and distributions of the residual lignin and hemicellulose, the formation of pores and voids in the bleached pulp, the fibril length and diameter, and the aggregation of fibrils (Treimanis, 1996). A higher pulping and bleaching severities lead to a pulp of a higher accessibility and reactivity (Ye and Farriol, 2005b). A higher accessibility and reactivity of pulps facilitate and improve the diffusion and penetration of methylation regents in the cellulose. The velocity of diffusion and penetration is lower than that of methylation (Brandt, 1986). Therefore, the diffusion and penetration is the control factor of the topochemical methylation. Thus, more cellulose molecules will participate in the methylation and a higher degree of substitution (DS) of methylcellulose will be synthesized from a pulp produced by a higher pulping severity (Ye and Farriol, 2005b).

Table 54 lists the condition of impregnation and the DS of methylcelluloses prepared from summer cardoon. When the concentration of NaOH solution and temperatures of impregnation increased, the DS of synthesized methylcelluloses also increased.

Table 54. Effect of impregnation on DS of summer cardoon methylcelluloses

NaOH concentration (%)	Temperature (^{0}C)	DS_2	DS_3	DS_6	DS
30	60	0.38	0.15	0.12	0.65
30	20	0.37	0.12	0.10	0.59
20	60	0.32	0.11	0.09	0.52
20	20	0.28	0.10	0.08	0.46

Table 55 lists the DS of methylcelluloses prepared from eucalyptus. These methylcelluloses were completely dissolved in dimethyl sulphoxide (DMSO) and partially dissolved in distilled water and 4% NaOH solution. When the cooking time and temperature increased, the degrees of substitution also increased. The reactivities at the third and sixth hydroxyl groups were almost similar. The reactivity at the second hydroxyl group was greater than that at the third and sixth hydroxyl group. The reactivity at the second hydroxyl group increased with the increase of cooking time and temperature. The reactivities at the third and sixth hydroxyl groups also increased with the increase of cooking time and temperature.

Table 55. DS of eucalyptus methylcelluloses

Cooking time (min)	Cooking temperature (^{0}C)	DS_2	DS_3	DS_6	DS
8	180	0.38	0.22	0.16	0.76
16	180	0.41	0.20	0.20	0.81
24	180	0.44	0.21	0.21	0.86
16	190	0.40	0.19	0.23	0.82
24	190	0.53	0.28	0.26	1.07

The residual lignin and hemicellulose, which adhered onto the cellulose fibrils, were eliminated much more by a higher cooking time and temperature (Patt et al., 1986). The disappearance of partial lignin and hemicellulose left some vacant space, which further formed voids and caused more accessible surfaces for methylation reagents to reach the interior of cellulosic fibers (Ye and Farriol, 2005b). Therefore, a higher cooking temperature and a longer cooking time would lead to a higher degree of substitution of methylcellulose.

4.6.2. Effect of methylation conditions

The methylation condition is the most important parameter of the production of methylcelluloses. Croon found that the methoxyl groups of methylcelluloses prepared by methyl chloride distributed much more homogeneously than the methoxyl groups of methylcelluloses prepared by dimethyl sulfate (Croon, 1951). Since iodomethane has much lower reactivity than chloromethane and dimethyl sulfate, the methylcelluloses prepared by iodomethane has much more uneven distribution of methoxyl groups on the methylcellulose chain. An increase of the concentration of mercerization NaOH solution caused an increase of the degree of substitution of the synthesized methylcelluloses (Krassig, 1993).

The methylation of dissolving pulps is a topochemical heterogeneous reaction (Ye and Farriol, 2005b). The low diffusion velocity of methylation reagents hinders the obtaining of a higher degree of substitution. Hence, a sufficient longer methylation time is often used to obtain a higher degree of substitution. A higher methylation temperature is also used to improve the diffusion of reactants in the fibrous celluloses. In both the industrial production and the laboratory synthesis, the methylation reagents were often added as a excessive ratio of several mole times of AGU (glucose unit) of cellulose. In addition, the methylation temperature is usually set to be near the maximum temperature of the boiling point of the dilute solvent if the methylation is carried out in organic slurry.

Table 56 lists the degrees of substitution of methylcelluloses prepared from α-cellulose. With an increase of mole ratio of iodomethane and the glucose unit, the degrees of substitution increased. The degrees of substitution at the second hydroxyl group and the third hydroxyl group also increased with the increase of mole ratio.

Table 56. DS of α-cellulose methylcelluloses

Mole ratio of CH_3I/AHG*	DS_2	DS_3	DS_6	DS
9.03	0.48	0.32	0.25	1.05
13.54	0.50	0.39	0.27	1.16
18.06	0.52	0.36	0.29	1.17
22.57	0.56	0.36	0.36	1.28

*: Mole ratio of iodomethane and AHG (AHG stands for anhydroglucose).

4.6.3. Effect of the species

Annual plants are diverse. The chemical compositions, morphological structures, and cellulosic fibers also are various. Therefore, the dissolving pulps produced from annual plants had quite different characteristics for subsequent methylation. Table 57 lists the properties of five pulps of annual plants (flax, hemp, sisal, abaca and jute), which were produced by the soda/AQ pulping and ECF bleaching processes. In Table 57, the methylcelluloses were produced from their pulps by a same methylation condition. Cellulose, no matter is produced from whichever plant, has same chemical unit structure (Purve, 1956). However, its other structures and properties are quite different after pulping and bleaching processes, such as the molecular weight, the degree of polymerization, the fiber length and diameter, the morphological structure that is bound by strong hydrogen bonds and weak wan de Walls force. Different species, which have quite different chemical compositions and morphological properties (especially pentosan contents and fiber lengths), cause that the synthesized methylcelluloses have quite different degrees of substitution and other special properties.

Table 57. Properties of bleached pulps of some annual plants

	Flax	Hemp	Sisal	Abaca	Jute
Degree of polymerization	1165	948	998	1928	1413
Brightness (%)	83.3	85.4	89.3	88.1	73.9
Fiber length (mm)	1.8 – 6.2	2.1 – 6.3	1.8 – 4.5	3.3 – 6.8	1.5 – 3.7
DS	1.45			1.36	

4.6.4. Effect of pretreatments

The dried pulps used for cellulose derivatives are usually needed to be activated in order to increase their accessibilities and reactivities (Krassig, 1957). Physical and chemical pretreatments have been used to achieve this objective (Ye and Farriol, 2005b). The accessibilities and reactivities of cellulose pulps are influenced by the various structural parameters: voids and pores, aggregated fibrils, degrees of crystallinity, and hydrogen bond strengths. The hydrogen bonds bind the fibrils together, and cause the formation of cellulose crystals, in which only their surfaces are accessible (Timell and Purves, 1951). Four pretreatments had been used to improve the accessibility and reactivity of abaca pulp (Ye and Farriol, 2005b). The water soaking can rupture the hydrogen bonds by a solvation function and thus makes aggregated fibrils to be separated. Therefore, more accessible surface is produced. The preliminary mercerization and mercerization under 15 bars have two main functions: swelling of the fibrils and rupture of the hydrogen bonds that bind the crystalline cellulose together. The preliminary mercerization lasted longer than mercerization under 15 bars, therefore its effect of alkaline depolymerization and decrystallization was much higher. The steam explosion is a physical process, which tears the bigger fibrils to smaller fibrils by a sudden evaporation of high-pressure and high-temperature liquid in the interior of fibers (Ye and Farriol, 2005a). Thus the steam explosion creates much more voids, and increases much more accessible surfaces. The degree of substitution of abaca pulp methylcellulose was significantly improved by water soaking, mercerization under 15 bars, steam explosion and preliminary mercerization. The preliminary mercerization was the best one of all pretreatments to improve and to increase the degree of substitution of methylcellulose.

Table 58. DS of abaca methylcelluloses

Pretreatments	DS_2	DS_3	DS_6	DS
Non-pretreatment	0.12	0.05	0.09	0.26
Water soaking	0.33	0.16	0.23	0.72
mercerization under 15 bars	0.35	0.20	0.25	0.80
Steam explosion	0.39	0.29	0.34	1.02
Preliminary mercerization	0.55	0.36	0.45	1.36

4.7. Course of methylation of bleached pulps of annual plants

4.7.1. Mercerization of pulps

Mercer found that a strong sodium hydroxide solution shrank cellulose in width and length, which therefore became denser (Mercer, 1850). The NaOH solution penetrates and diffuses into the voids of bleached pulps. This process is shown in Figure 47. After absorbing some of the NaOH solution, the original fiber I developed into the larger fiber II. The diameter of fiber III was the largest because the capacity of absorption was the maximum. When the diffusion and mass transfer reached an equilibrium state, most fibers adjusted to become fiber IV.

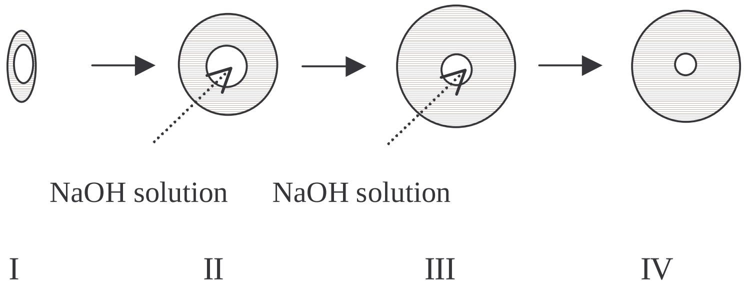

Figure 47. Swelling and diffusion during mercerization

The bleached pulp is impure cellulose. The bleached pulp usually contains more than 90% cellulose, which is a complex composite with both crystalline and amorphous structures (Krassig, 1993; Lai, 1996). During the mercerization, the crystalline area is attacked by the strong NaOH solution (Takai, 1977), which leads to the cellulose chain gradually being debonded from the crystal (Takai, 1977). Thus, amorphous regions are formed and developed by alkali attacking the outer surface of the crystal (Takai, 1977). The crystalline cellulose gradually develops into amorphous cellulose. During the mercerization, most of the cellulose gradually transfers its crystal lattice from cellulose I to Na-cellulose II; and some of the cellulose changes its crystal lattice from cellulose I to Na-cellulose I; the amorphous cellulose II to Na-cellulose II (Takai, 1977).

The excess alkali was pressed out at a press factor of 5. This press factor was higher than the traditional press factor, 3, which meant that the steam-exploded pulps had a greater capacity of absorption and that the pulps had more surfaces and voids. These steam-exploded pulps, then, were more accessible and reactive, which favored the following methylation.

4.7.2. Methylation of alkali cellulose

The methylation of alkali cellulose with a methyl halide is a nucleophilic substitution, which yields a rate-controlled distribution of methoxyl on the methylcellulose molecules (Timell and Purves, 1951; Brandt. 1986). In a heterogeneous organic reaction medium, the methylation is a rate determining transport process with chloromethane as the methylation reagent under high pressure (Timell and Purves, 1951). Under ambient pressure and with dimethyl sulfate and iodomethane as methylation agents, however, the methylation can be diffusion controlled (Timell and Purves, 1951; Brandt. 1986). The heterogeneous methylation is an intermicellar or topochemical reaction (Timell and Purves, 1951). The reagents initially penetrate into the amorphous regions between the crystalline cellulose micelles. This penetration continues during the methylation from the surface to the inner regions of the micelles. The reaction of cellulose and iodomethane or dimethyl sulfate is faster than the diffusion. Thus, the total methylation speed is determined by diffusion (Timell and Purves, 1951).

4.7.3. Effect of the bleached pulps

The methylation of bleached pulps is a heterogeneous reaction in organic slurry. The cellulose pulp is a fibrous solid making up with a lot of dispersed or aggregated microfibrils, in which the cellulose consists of fibrils, microfibrils and the smallest elementary fibrils in the matrix of residual lignins and residual hemicelluloses (Osullivan, 1997). In the elementary fibrils, crystalline and amorphous cellulose coexist and have completely different accessibilities and reactivities. It is well known that the cellulose crystals have very little accessibility. The crystalline cellulose, which partially remains the order structure after mercerization, only has its surface to be accessible by the methylation reagents in the initial stage of methylation (Brandt, 1986). The crystalline cellulose is gradually attacked and ruptured by the concentrated alkaline solution in the proceeding of mercerization and methylation. The amorphous celluloses have quite different accessibilities depending on the species, the pulping conditions, the bleaching conditions and the drying conditions (Ye and Farriol, 2005b). The amorphous cellulose is partially accessible because strong hydrogen bond strength and weak van de Walls force aggregate the small fibrils to be bigger fibrils, which have inaccessible interior in the interiors of aggregated fibrils. These inaccessible interiors of fibrils are also attacked and ruptured by the concentrated alkaline solution in the proceeding of mercerization and methylation.

The surface of the fibrils of bleached pulps is of course more highly accessible and reactive than the interior is. The accessible part of the bleached pulps consists of the dispersed amorphous cellulose, the surface of the dispersed microfibrils or elementary fibrils, the surface of aggregated amorphous cellulose, the surface of the crystalline cellulose of the dispersed microfibrils, and the surface of the aggregated microfibrils. The accessible part of the bleached pulps is assumed to react much more easily than the inaccessible part. The methylation agents are assumed to diffuse and penetrate more quickly in the assessable part. This unbalanced accessibility causes a non-uniform distribution of the substituted methylcellulose in the methylation of the bleached pulps. Not only the distribution of substituted methylcelluloses or un-substituted celluloses is random, but also the distribution of methoxyl groups on the methylcellulose molecule chain is also random. In addition, the distribution of methoxyl group on a single AGU is also random. These assumptions are further confirmed by our data of the molecular weights and degrees of substitution of synthesized methylcelluloses (Ye et al., 2004a, b; Ye and Farriol, 2005a, b). The methylcelluloses had higher molecular weights and degree of substitution if they are synthesized from pulps of higher accessibilities (Ye and Farriol, 2005b).

According to this topochemical assumption, the defibrillation of pulping is essential for the subsequent methylation. Thus, a better effect of impregnation and a higher p-factor of cooking will cause a pulp of less aggregated microfibrils, more disintegrated microfibrils, smaller diameters of microfibrils, and more voids in the microfibrils. Thus, the accessible parts of the pulps are increased and the reactivities of the pulps are improved.

The residual lignin and hemicellulose coexist and distribute randomly in the cellulose because of incomplete pulping and bleaching. The residual lignin and hemicellulose adhere on the surface of the cellulose (Osullivan, 1997), causing the difficulty of diffusion and penetration of the chemical reagents onto the surface of the cellulose. The residual lignin and hemicellulose also can compete with cellulose to react with alkali and methylating reagents. The crystalline cellulose of course has less reactivity than lignin and hemicellulose have. The residual lignin and hemicellulose consume some alkali. The methylation needs to be remained with a certain concentration of alkaline solution in the reaction medium (Brandt, 1986). Thus, when the concentration of alkaline solution is as low as the limit concentration, the gradual consumption and reduction of alkali cause the stop of the proceeding of methylation process. The annual plant pulps usually have higher contents of hemicellulose. The residual hemicellulose as well as residual lignins consumes a part of alkaline and methylation reagents, which leads to synthesized methylcelluloses with lower degrees of substitution. Therefore, the less contents of the lignin and hemicellulose in the bleached pulps will cause the better accessibilities and reactivities of the bleached pulps, and further better properties of synthesized methylcelluloses (Ye and Farriol, 2005b).

4.7.4. Factors influencing the properties of methylcelluloses

During impregnation, a longer retention time and a higher concentration of the NaOH solution showed that the pretreatment had a beneficial effect on the 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 the cooking, a higher p-factor demonstrated a better effect of defibrillation, removed more lignin and hemicellulose, and created more voids in the microfibrils. A better-cooked pulp led to a better accessibility and reactivity of the cellulose and therefore a better synthesized methylcellulose.

A plant species has an inherent fiber morphology and an inherent chemical composition. Inherent properties are essential factors to consider when preparing methylcelluloses, 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 synthesized methylcelluloses. Even with the same species, different harvest times influence the properties of synthesized methylcelluloses. Different pulp accessibilities and reactivities 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 of synthesized methylcelluloses.

5. Conclusions

A novel facile methylation method was developed. The methylation of α-cellulose, miscanthus, cardoon, and eucalyptus had proved this method. The methylcelluloses, which were synthesized in an ordinary apparatus, had sufficient and different properties to compare plant species, and process parameters of pulping and bleaching. Therefore, this method is appropriate for evaluating whether certain plants could be used to produce methylcellulose.

It is feasible and appropriate to produce methylcelluloses from miscanthus, cardoon, and eucalyptus. As the added volumes of iodomethane increased, so did the DS and water-soluble contents. Most methylcellulose solutions in 4% NaOH and DMSO were Newtonian type. When the pulping severities increased, the DS and the water-soluble contents also increased while intrinsic viscosities and solution viscosities of methylcelluloses decreased. The pulping severity was one of the key factors in the production of pulps and methylcelluloses. However, the species was a decisive factor for the preparation of methylcelluloses. Cardoon easily provided high quality pulps and was suitable for synthesizing high molecular weight methylcelluloses. Miscanthus was suitable for synthesizing methylcelluloses with a high degree of substitution. Eucalyptus was suitable for synthesizing methylcelluloses with high purities and degrees of substitution.

Flax, hemp, abaca, jute and sisal pulps had low accessibilities. Most of the amorphous celluloses in the pulps were inaccessible before pretreatment. After preliminary mercerization, the intrinsic viscosity, mean hydrogen strength and relative crystallinity index of the pulps decreased, which improved their accessibilities and reactivities. Water soaking, pre-mercerization, mercerization under 15 bars of pressure, and steam explosion increased the accessibility and reactivity of the abaca pulp. These pretreatments have different effects on different celluloses of annual plants, which indicates that species is the main influencing factor.

It is also feasible and appropriate to produce methylcelluloses from the bleached flax, hemp, sisal, jute, and abaca pulps. Each methylcellulose synthesized from these ECF bleached pulps was a mixture of methylcelluloses of different DS. The flax was the best raw material to produce methylcellulose. The preliminary mercerization of pulps improved the properties of the synthesized methylcelluloses. The preliminary mercerization had a different effect on each pulp species. The water soak, preliminary mercerization, mercerization under 15 bars and steam explosion improved the properties of the abaca methylcelluloses. The steam explosion was the best pretreatment for the abaca pulp.

A higher alkali charge and a longer time in the impregnation led to lower Mw and higher DS of spring cardoon methylcelluloses. The impregnation conditions had little influence on the Mw and DS of summer cardoon methylcelluloses. The Mw and DS of miscanthus methylcelluloses increased with the increase of cooking time. A shorter cooking time with a lower cooking temperature caused a higher Mw and a lower DS of the eucalyptus methylcellulose. The studied pretreatments increased Mw and DS of methylcelluloses of abaca, flax, sisal, jute, and hemp. The species decisively influences Mw, DS, and effect of pretreatment.

The water-soluble methylcelluloses with intermediate molecular weights were prepared from juvenile eucalyptus and annual plants. The effect that the impregnation times, the impregnation temperatures, the alkali charge of impregnation, the cooking times, the pulping severity, the pretreatments and the charge of methylation reagents have on the molecular weights of synthesized methylcelluloses depends on the species. The present research shows that the species is a decisive factor in the production of methylcellulose. However, the pulping, the cellulose pretreatments and the methylation conditions can adjust the molecular weights and degrees of substitution of the synthesized methylcellulose. Therefore, the present research may be used to control and optimize the quality of methylcelluloses prepared from annual plants.

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