

Preparation of Cellulose Acetate Produced from Lignocellulosic Biomass¹

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ABSTRACT

Cellulose acetate is one of well-known industrial materials which have various commercial uses. We treated the lignocellulosic biomass using two-step (steam explosion-chemical) reaction followed by acetylation to get the cellulose acetate in this study. The two-step treatment was done to improve the yields of acetylation of the substrates. The yields of the cellulose acetate were about 88.4, 88.1, and 151.7% in barley straw, rice straw, and oak tree, respectively. Also the degree of substitution (DS) of the acetates was 2.1 to 2.5 in the biomass. We found that the biomass were valuable cellulosic sources, including their derivatives, in this study. This means that the biomass can be converted into the high-valued cellulosic stuff.

Keywords : cellulose acetate, lignocellulosic biomass, steam explosion, two-stage treatment, acetylation

1. INTRODUCTION

Sources of biomass-based renewable energy, such as cellulosic ethanol, are considered as one solution to the energy crisis and global warming. Agricultural and forestry biomass are major sources of cellulosic ethanol (Hess *et al.*, 2007).

Cellulose is the major components of plant biomass; it is readily available and does not compete with the food supply. Cellulose is considered a long-term, renewable alternative to

fossil fuel (Van de Vyver *et al.*, 2011).

Cellulose acetate has been widely used in the textile industry, as raw material in lacquer production, and in the manufacture of plastics, filter tow, films, membranes, LCDs, and others (Amin and Shahjehan, 1999; Edgar *et al.*, 2001). The properties of the cellulose acetates used are very important for these applications. In recent years, the low-cost lignocellulosic biomass has become attractive as a renewable resource because it is available in large quantities and is routinely cultivated worldwide.

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Wood pulp and cotton linters are the major sources of all cellulose derivatives (Majewicz and Padlas, 1979), whereas few reports are available on the preparation of cellulose acetate from rice straw (Fan *et al.*, 2013), corn stalk (Biswas *et al.*, 2006), sugarcane bagasse (Shaikh *et al.*, 2009), and newspaper (Filho *et al.*, 2008). Industrially, cellulose acetates are often produced by reacting cellulose with an excess of acetic anhydride in the presence of sulfuric or perchloric acid as catalysts (Hummel, 2004). Cellulose acetate with a degree of substitution (DS) value of about 2.5 is a well-established technical product. Therefore, a need exists to explore greener methods to prepare partially substituted cellulose acetates and those with DS values ranging from 2.2 to 2.7 (Heinze and Liebert, 2001).

Steam explosion has been applied commercially to hydrolyze hemicellulose, in which high pressure steam explosion applied on wood chips in a large vessel without chemicals for several minutes, and then some steam is rapidly vented to reduce the pressure while the biomass is discharged into a large vessel for flash cooling (Fernández-Bolaños *et al.*, 2001). In this process, steam is used to promote hydrolysis of hemicellulose, and the process is terminated by explosive decompression. Water itself may also act as an acid at high temperature. The expansion at the end of pretreatment terminates the reaction and opens up the particulate structure of wood. The removal of hemicellulose increased pore volume and reduced particle size (Cristóbal *et al.*, 2006).

We are exploring at agricultural and forestry byproducts as sources of materials with higher value product. Barley straw, rice straw and oak wood are currently used as roughage in animal feed, as mulch, and as a substrate for mushroom production. Additionally, those material are readily available and inexpensive.

In this study, we attempted to convert cellulose isolated from agricultural and forestry byproducts to cellulose acetate. In the present work, we developed a two-stage treatment (steam explosion-chemical treatment) for extracting cellulose from lignocellulosic biomass and converting it into cellulose acetate. Additionally, the properties of the resultant cellulose acetate were thoroughly investigated.

2. MATERIALS and METHODS

2.1. Materials

Barley straw (*Hordeum vulgare*), rice straw (*Oryza sativa*) and oak wood (*Quercus mongolica*) used in this study were obtained from the Korea Forest Research Institute; all raw materials were cut to an average size of 2 - 3 cm for steam explosion pretreatment. The raw materials and cellulose isolated from barley straw, rice straw and oak wood was milled to 1 - 2 mm and then sieved through a -20 mesh/ +80 mesh screen and collected for chemical composition analysis as described below.

2.2. Two-stage treatment of barley straw, rice straw and oak wood

2.2.1 Steam explosion treatment (first stage)

Steam explosion treatment, which was used as a physicochemical pretreatment, was carried out in a batch pilot unit equipped with a 100 ℓ reaction vessel. The “severity factor” (Ro) was used to map the destruction, desegregation, and depolymerization of barley straw, rice straw and oak wood. Ro was calculated using the following relationship (Fernández-Bolaños *et al.*, 2001):

$$Ro = \{t \times \exp[(T-100)/14.75]\} \dots\dots\dots \text{Eq. (1)}$$

where T is the temperature (°C) and t the time (min). A steam temperature of 213°C and pretreatment time of 3 min were applied to realize a severity factor value of $\log Ro = 3.80$. After the saturated steam exposure, a ball valve at the bottom of the reactor was opened suddenly to bring the reactor rapidly to atmospheric pressure. The steam exploded material was recovered in a cyclone and after cooling to about 40°C filtered for solid recovery. The solid fraction was for used chemical treatment (second stage treatment).

2.2.2 Chemical treatment (second stage)

Hot water treatment was carried out at 80°C in a soxhlet extraction at 100 rpm for 1 h. Five grams of dry biomass was weighed into 250 ml Erlenmeyer flasks, to which 160 ml of distilled water was then added. After the reaction,

Table 1. Oxygen - alkali conditions

Composition	Condition
Sample weight (g)	2
NaOH concentration (%)	6
Reaction time (hour)	2
Reaction temperature (°C)	200
O ₂ -pressure (kgf/cm ²)	10

the liquid was separated from the solid.

Sodium chlorite-acetic acid treatment was carried out at 70°C in a water bath with an initial liquid-to-solids ratio of 32. Five grams of dry biomass was weighed into 250 ml Erlenmeyer flasks, and then 160 ml of distilled water was added followed by 0.6 g/g of dry biomass of sodium chlorite (NaClO₂) and 0.6 ml/g dry biomass of acetic acid. The slurry was thoroughly mixed by shaking the flasks, and then a 50 ml Erlenmeyer flask was inverted over the neck of the reaction flask. The flasks were incubated in a fume hood at 70°C with intermittent mixing, and fresh charges of sodium chlorite and acetic acid were added to the reaction every 2 h for up to 8 h.

Oxygen-alkali treatment was carried out in a Quantum high intensity mini mixer using the conditions shown in Table 1. After cooking, as well as after oxygen-alkali treatment, the liquid was separated from the solid and the solid was thoroughly washed. These delignification stages were performed according to the methods of Vu *et al.* (2004), who have described the pulping and delignification processes, including the washing procedure, in detail.

2.3. Preparation of cellulose acetate

Acetylation was performed on the reaction product of steam exploded - chemical treated barley straw, rice straw and oak wood. Two grams of sample along with 0.5 g of acetic acid, 5.0 g of acetic anhydride, and 0.04 g of sulfuric acid was added to 100 ml round bottom flask. The mixture was heated to 40°C while stirring with a magnetic stirrer. After 3 h, the reaction mixture was allowed to cool to room temperature, with the filtrate being collected in a large beaker. Methyl alcohol was added and the mixture was stirred overnight at room temperature and then filtrated. The cellulose acetate was collected on the filter paper, placed in evaporating dishes and dried at 80°C in a vacuum oven overnight.

2.4. Analytical Methods

Ash content was determined after combustion of the samples at 525°C for 4 h. Extractive content was determined as the solubilized material after soxhlet extraction with ethanol for 24 h. Lignin content was assessed gravimetrically as Klason lignin. Sugar composition was determined using the alditol acetate method (Voiges *et al.*, 2012). The sample was hydrolyzed using a two-stage procedure: 1) 12 M H₂SO₄ (200 μl) for 1 h at room temperature and 2) 1 M H₂SO₄ (attained by adding 1.8 ml distilled water to the tube) for 1 h at 121°C. Acetylation was performed at room temperature (10 min) with 1-methylimidazole (200 μl) and

1 ml of acetic anhydride and 5 ml of double distilled water was added to quench the reaction. The cellulose and hemicellulose contents were calculated using Eq. (2) and (3), where 0.90 and 0.88 is the correction coefficient for hydration:

$$\text{Cellulose (\%)} = \frac{\text{glucose released (g)} \times 0.9}{\text{sample dry weight (g)}} \times 100 \quad \text{Eq. (2)}$$

$$\text{Hemicellulose (\%)} = \frac{(\text{arabinose} + \text{xylose released (g)} \times 0.88) + (\text{mannose} + \text{galactose released (g)} \times 0.9)}{\text{sample dry weight (g)}} \times 100 \quad \text{Eq. (3)}$$

2.5. Characterization of cellulose acetate

The alpha cellulose content was determined according to JIS P-1801. DS value was determined by a complete hydrolysis of the samples with sodium hydroxide (Filho *et al.*, 2008) and the degree of polymerization (DP) value was determined by viscosity measurement of the samples dissolved in copper-ammonium hydroxide solution (Cao *et al.*, 2007).

Fourier transform infrared spectroscopy (FTIR) was carried out on a Mattson Instruments Inc. Galaxy 7020A spectrometer in the range of 4000 - 400 cm⁻¹. Solid samples were ground with dried KBr powder, and compressed into a disc prior to analysis.

Table 2. Chemical composition of barley straw, rice straw and oak wood^a

Chemical composition	Dry matter (%)		
	Barley straw	Rice straw	Oak wood
Cellulose	39.8	37.6	48.0
Hemicellulose ^b	26.2	23.6	16.2
Xylose	18.7	16.5	11.4
Galactose	2.1	0.6	3.8
Arabinose	3.6	0.4	0.7
Mannose	1.8	6.1	0.3
Lignin	13.3	19.3	24.2
Extractives	5.1	9.0	5.7
Ash	8.9	11.5	2.9

^a Data in the table are based on oven dry samples

^b Hemicellulose : xylose + galactose + arabinose + mannose

3. RESULTS and DISCUSSION

3.1. Chemical composition of barley straw, rice straw and oak wood

The chemical composition of barley straw, rice straw and oak wood is presented in Table 2. Chemical analysis demonstrated significant differences between the different materials. Barley straw, rice straw and oak wood were found to contain 39.8%, 37.6% and 48.0% cellulose, respectively. Additionally, the hemicellulose content of barley straw, rice straw and oak wood was 26.2%, 23.6% and 16.2%, respectively. Hemicellulose content (arabinose, xylose, mannose and galactose) in barley straw was higher than that in rice straw and oak wood. However, the carbohydrate (cellulose and hemicellulose) content, of barley straw (66.0%), rice straw (61.2%) and oak wood (64.2%) assessed in this study was similar. This content is higher than that in other sources of lignocellu-

losic biomass, such as poplar (58.6%) (Kumar *et al.*, 2009), rice straw (53.4%) (Chen *et al.*, 2011), wheat straw (48.9%) (Ballesteros *et al.*, 2006) and sweet sorghum bagasse (41.8%) (Li *et al.*, 2010). The lignin content differed significantly among barley straw, rice straw and oak wood, ranging from 13.3% to 24.2%. The lignin content of oak wood (24.2%) was higher than that of agricultural residue (barley straw and rice straw).

Extractive content was greatest in rice straw (9.0%), followed by that in oak wood (5.7%) and then by that in barley straw (5.1%). Ash was also greatest in rice straw (11.5%), followed by that in barley straw (8.9%) and then by that in oak wood (2.9%).

The differing chemical compositions may be due to the differences in the kind, the cultivation climate and the harvest season. Agriculture and forest residue, such as barley straw, rice straw, and oak wood is a promising option for feedstock for cellulose or cellulose

Table 3. Chemical composition of barley straw, rice straw and oak wood after steam explosion - chemical treatment

Species	Treatment	Yield (%)	Lignin (%)	α -cellulose (%)	D.P. ^a
Barley straw	Steam explosion / Hot water	63.3	39.0	76.4	866.7
	Steam explosion / Sodium chlorite-acetic acid	62.8	11.5	68.9	288.8
	Steam explosion / Oxygen-alkali	38.9	10.1	74.5	288.8
Rice straw	Steam explosion / Hot water	77.6	35.7	81.4	841.5
	Steam explosion / Sodium chlorite-acetic acid	72.9	21.5	67.7	254.6
	Steam explosion / Oxygen-alkali	40.5	5.3	78.3	271.7
Oak wood	Steam explosion / Hot water	76.3	28.9	84.7	934.1
	Steam explosion / Sodium chlorite-acetic acid	70.5	18.5	67.1	442.7
	Steam explosion / Oxygen-alkali	59.5	10.8	83.0	604.2

^a Degree of polymerization

acetate production, especially in terms of their abundant availability, low cost and yield.

3.2. Chemical composition of steam exploded – chemical treated barley straw, rice straw and oak wood

Barley straw, rice straw and oak wood were treated using steam explosion and chemical treatment (hot water, sodium chlorite - acetic acid and oxygen - alkali) described in section 2.2.

The yield, lignin content, α -cellulose content and DP of the insoluble residue recovered by filtration after steam explosion-chemical treatment (hot water, sodium chlorite - acetic acid and oxygen - alkali) can be seen in Table 3.

The yield, lignin content, α -cellulose content and DP in of the steam explosion / hot water treated insoluble residue were higher than that treated using other processes. However, as the steam explosion / hot water treated insoluble residue possessed fairly high lignin content, it

is not very suitable for cellulose derivative synthesis. In addition, the presence of lignin reduces the accessibility of the hydroxyl group of cellulose (Ueda *et al.*, 1988). Yield and lignin content were lowest in the steam explosion / oxygen - alkali treated insoluble residue. The loss in yield during steam explosion / oxygen - alkali process was probably due to the conversion of hemicellulose and lignin into soluble fragments.

α -cellulose content is an important parameter for the production of cellulose acetate and indicates the extent of hemicellulose removal. Cellulose acetate is usually prepared from cellulose with high α -cellulose contents (more than 95 %) such as purified cotton linters and wood pulps (Hamed *et al.*, 2015). However, the α -cellulose content of the steam explosion - chemical treated barley straw, rice straw and oak wood ranged from 67.1 to 84.7 %. The α -cellulose content of steam explosion / sodium chlorite-acetic acid (67.1 - 68.9%) treated resi-

Table 4. Sugar composition of barley straw, rice straw and oak wood after steam explosion - chemical treatment

Species	Treatment	Arabinose	Xylose	Mannose	Galactose	Glucose
Barley straw	Steam explosion / Hot water	1.0	10.4	2.2	- ^a	86.4
	Steam explosion / Sodium chlorite-acetic acid	-	2.9	0.6	-	96.6
	Steam explosion / Oxygen-alkali	-	1.7	0.9	-	97.4
Rice straw	Steam explosion / Hot water	-	7.2	-	-	92.8
	Steam explosion / Sodium chlorite-acetic acid	0.4	2.6	6.1	-	90.9
	Steam explosion / Oxygen-alkali	-	1.6	0.6	-	97.8
Oak wood	Steam explosion / Hot water	-	13.3	2.8	-	83.9
	Steam explosion / Sodium chlorite-acetic acid	0.9	10.0	5.0	-	84.1
	Steam explosion / Oxygen-alkali	-	2.6	1.2	-	96.2

^a Not detected

due was lower of residues treated using steam explosion / hot water (76.4 - 84.7%) or steam explosion / oxygen-alkali (74.5 - 83.0%).

The DP was the lowest in the steam explosion / sodium chlorite-acetic acid treated insoluble residue. The steam explosion / sodium chlorite-acetic acid process reportedly has a tendency to reduce the molecular weight and DP of cellulose (Kumar *et al.*, 2009), which is most likely to be the result of acid hydrolysis and oxidative cleavage of the polymer chain.

The sugar composition of the insoluble residue recovered by filtration after steam explosion-chemical treatment (hot water, sodium chlorite-acetic acid and oxygen - alkali) can be seen in Table 4. When compared with the steam explosion / hot water treatment, both steam explosion / sodium chlorite - acetic acid and steam explosion / oxygen - alkali treatment decrease xylose content. Galactose was completely removed at steam explosion / hot water, steam explosion / sodium chlorite-acetic acid and steam explosion / oxygen - alkali treatment.

The maximum glucose content was attained when using steam explosion / oxygen - alkali treatment.

3.3. Characterization of the produced cellulose acetate

The yield, DP, DS, and sugar composition of the cellulose acetate obtained from barley straw cellulose acetate, rice straw cellulose acetate and oak wood cellulose acetate were given in Table 5.

The amount of xylose and mannose resulted in the lowered yield acetylated from oak wood. Mannose and xylose are representative neutral monosaccharides contained as hemicellulose in wood pulp, and derived from glucomannan and xylan, respectively. Glucomannan acetate has often been reported to be a major cause of false viscosity and poor filterability of cellulose acetate, while xylan acetate was a major cause of haze, poor filterability, and coloring (He *et al.*, 2007).

Table 5. Characterization of cellulose acetate obtained from steam explosion - chemical (Steam explosion / Oxygen-alkali) treated barley straw, rice straw and oak wood

Species	Yield (%)	D.P ^a	D.S ^b	Sugar composition (%)				
				Arabinose	Xylose	Mannose	Galactose	Glucose
Barley straw	88.4	> 186	2.2	- ^c	1.7	0.9	-	97.4
Rice straw	88.1	> 186	2.1	-	0.8	3.2	-	96.0
Oak wood	151.7	> 186	2.5	-	0.7	0.8	-	98.5

^a Degree of polymerization^b Degree of substitution^c Trace, below 0.1%

Cellulose acetates with various DS values in the range from 2.1 to 2.5 were obtained by species, while DP was greater than 186 (Table 5). Cellulose acetate with a DS of about 2.5 is a well-established technical product processed to fibers, filter tow, membranes, and thermo-plastic materials (Schaller *et al.*, 2013).

Fig. 1 - Fig. 3 shows the FTIR spectra of the three samples in the fingerprint region between 4000 and 400 cm^{-1} , corresponding to cellulose acetate acetylated from barley straw, rice straw and oak wood cellulose. The main alterations are found at the region from 3500 to 2500 cm^{-1} and from 1800 to 600 cm^{-1} .

The assignment for each of these absorption bands may be seen in detail in Table 6. Some linkages are considered specific to lignin and extractives (e.g. C₁ component related to -C-H and -C-C), while some to cellulose and hemicellulose (e.g. C₂ and C₃ related to -C-O and -C=O) (Colom *et al.*, 2003). Another important aspect observed in the spectrum of the cellulose acetate acetylated from rice straw cellulose is the decreasing absorption intensity of the band located at around 3400 cm^{-1} assigned to the stretching of the hydroxyl group when com-

pared with the spectra of cellulose acetate acetylated from barley straw and oak wood cellulose. This occurs because the hydroxyl groups are replaced by acetyl groups in the reaction and the pattern of the cellulose spectrum corroborates the DS value for a cellulose acetate (Table 5).

The absorption band at 1641 cm^{-1} was not observed on the spectrum of the cellulose acetate acetylated from barley straw cellulose. This absorption was attributed to the functional groups present in the lignin associated with barley straw cellulose before the delignification process. Another important aspect at this region of the infrared spectrum is that, in the spectrum for cellulose acetate acetylated from barley straw cellulose, the band at approximately 800 cm^{-1} is not observed, while it is seen in the spectra of cellulose acetate acetylated from rice straw and oak wood cellulose. The small sharp band at 802.74 and 800.81 cm^{-1} in the spectra shown in Fig. 2 and Fig. 3 are attributed to β -glucosidic linkages between the sugar units in hemicelluloses and celluloses (Colom *et al.*, 2003; and Adebajo and Frost, 2004).

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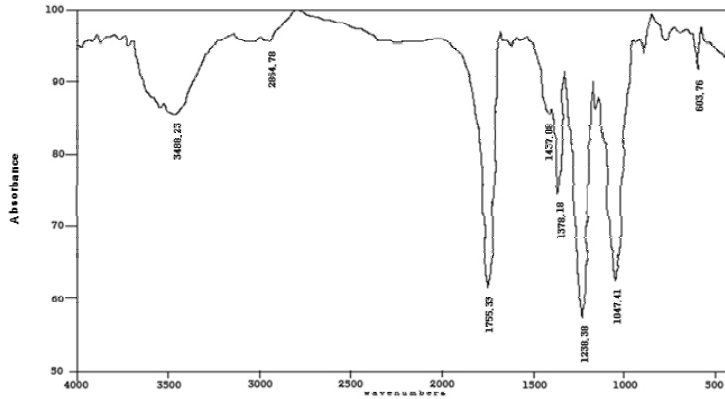


Fig. 1. FTIR spectrum of cellulose acetate obtained from steam explosion - chemical (steam explosion/oxygen-alkali) treated barley straw.

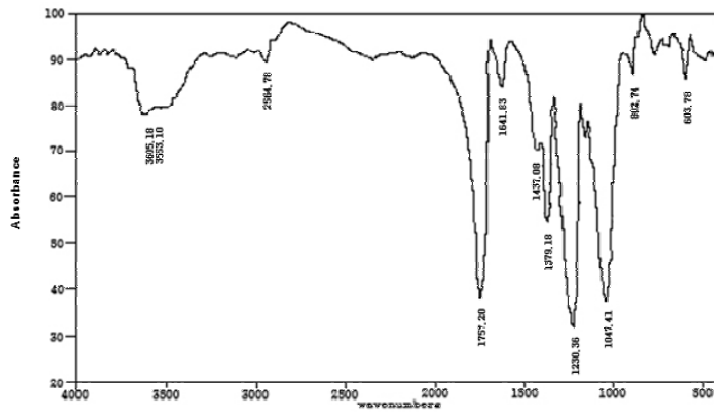


Fig. 2. FTIR spectrum of cellulose acetate obtained from steam explosion - chemical (steam explosion/oxygen-alkali) treated rice straw.

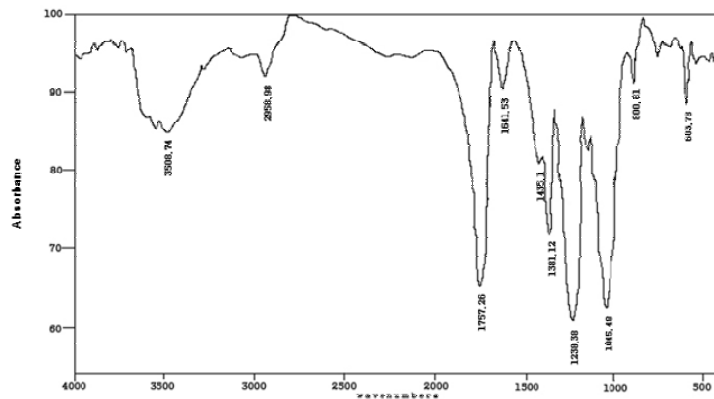


Fig. 3. FTIR spectrum of cellulose acetate obtained from steam explosion - chemical (steam explosion/oxygen-alkali) treated oak wood.

Table 6. Assignments of main absorption bands in cellulose acetate (Colom *et al.*, 2003 and Adebajo and Frost, 2004)

Wave number (cm ⁻¹)			Assignment
Barley straw	Rice straw	Oak wood	
3488.23	3553.10	3508.74	OH stretching
2864.78	2564.78	2958.98	CH stretching of CH ₂ and CH ₃ groups
1755.33	1757.20	1757.26	C=O stretching of acetyl or carboxylic acid
	1641.83	1641.53	C=C stretching of aromatic ring
1437.08	1437.08	1435.10	CH ₂ bending
1378.18	1379.18	1381.12	C-H deformation
1238.38	1230.36	1238.38	C-O stretching of acetyl group
1047.41	1047.41	1045.48	C-O stretching in cellulose, hemicellulose
	802.74	800.81	β -Glucosidic linkages
603.76	603.78	603.78	OH out-of-plane bending and/or atmospheric CO ₂ (deformation vibration) contamination

4. CONCLUSION

Cellulose was separated from barley straw, rice straw and oak wood by steam explosion pretreatment with chemical treatment successively, and it was further acetylated in the presence of acetic anhydride and acid catalyst. The removal of hemicellulose and lignin was carried out in steam explosion / hot water, steam explosion / sodium chlorite-acetic acid and steam explosion / oxygen-alkali treatment. The acetylation of cellulose derived from barley straw, rice straw and oak wood was investigated using DP, DS, FTIR. Cellulose acetate with DS value around 2.1 - 2.5 was obtained from barley straw, rice straw and oak wood. The removal of hemicellulose and lignin from barley straw, rice straw and oak wood, and the formation of cellulose acetate were confirmed by FTIR.

Cellulose of lignocellulosic biomass was

converted in a quantitative yield into cellulose acetate under mild conditions by carrying the acetylation reaction at room temperature. The cellulose acetate (DS 2.5) made from oak wood could be suitable for fibres, filter tow, membranes and thermoplastic materials.

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REFERENCES

- Adebajo, M.O., Frost, R.L. 2004. Infrared and ¹³C MAS nuclear magnetic resonance spectroscopic study of acetylation of cotton. *Spectrochimica Acta Part A*, 60: 449.
- Ahmed, A., Adnot, A., Kaliagnine, S. 1987. ESCA study of the solid residues of supercritical extraction of *Populus tremuloides* in methanol.

- Journal of Applied Polymer Science 34 (1): 359~375.
- Amin, M.N., Shahjehan, M.D. 1999. Production of cellulose acetate from jute sticks. Pakistan Journal of Scientific and Industrial Research 42: 377~379.
- Ballesteros, M., Negro, Oliva, J.M., Cabanas, A., Manzanares, P., Ballesteros, M. 2006. Ethanol production from steam explosion pretreated wheat straw. Applied Biochemical Biotechnology 130: 278~288.
- Biswas, A., Shah, B.C., Lawton, J.W., Willett, J.L. 2006. Process for obtaining cellulose acetates from agricultural by-products. Carbohydrate Polymers, 64: 134~137.
- Cao, Y., Wu, J., Meng, T., Zhang, J., He, J., Lia, H., Zhanga, Y. 2007. Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). Carbohydrate Polymers 69(4): 665~672.
- Chen, W.H., Pen, B.L., Yu, C.T., Hwang, W.S. 2011. Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute-acid and steam explosion for bio-ethanol production. Bioresource Technology 102: 2916~2924.
- Colom, X., Carrillo, F., Nogues, F., Garriga, P. 2003. Structural analysis of photodegraded wood by means of FTIR spectroscopy. Polymer degradation and Stability 80: 543~549.
- Cristóbal, C., Encarnación, R., Ignacio, B., María, J.N., Eulogio, C., 2006. Enhanced enzymatic hydrolysis of olive tree wood by steam explosion and alkaline peroxide delignification. Process Biochemistry 41: 423~429.
- Edgar, K.J., Buchanan, C.M., Debenham, J.S., Rundquist, P.A., Seiler, B.D., Shelton, M.C., Tindall, D. 2001. Advances in cellulose ester performance and application. Progress in polymer science 26(9): 1605~1688.
- Fan, G., Wang, M., Liao, C., Fang T, Li, J., Zhou, R. 2013. Isolation of cellulose from rice straw and its conversion into cellulose acetate catalyzed by phosphotungstic acid. Carbohydrate Polymers 94(1): 71~76.
- Fernández-Bolaños, J., Felizón, B., Heredia, A., Rodríguez, R., Guillén, R., Jiménez, A. 2001. Steam explosion of olive stones: hemicellulose solubilization and enhancement of enzymatic hydrolysis of cellulose. Bioresource Technology 79: 53~61.
- Filho, G.R., Monteiro, D.S., Meireles, C.S., de Assunção, R.M.N., Cerqueira, D.A., Barud, H.S. 2008. Synthesis and characterization of cellulose acetate produced from recycled newspaper. Carbohydrate polymers, 73: 74~82.
- Hamed, O.A., Jodeh, S., Al-Hajj, N., Hamed, E.M., Abo-Obeid, A., Fouad, Y. 2015. Cellulose acetate from biomass waste of olive industry. Journal of Wood Science 61: 45~52.
- He, J., Cui, S., Wang, S. 2007. Preparation and crystalline analysis of high-grade bamboo dissolving pulp for cellulose acetate. Journal of Applied Polymer Science 107(2): 1029~1038.
- Heinze, T., Liebert, T. 2001. Unconventional methods in cellulose functionalization. Progress in Polymer Science 26(9): 1689~1762.
- Hess, J.R., Wright, C.T., Kenney, K.L. 2007. Cellulosic biomass feedstocks and logistics for ethanol production. Biofuels, Bioproducts and biorefining 1(3): 181~190.
- Hummel, A. 2004. Acetate manufacturing, process and technology 3.1 industrial processes. Macromolecular Symposia 208: 49~60.
- Kumar, R., Mago, G., Balan, V., Wyman, C.E. 2009. Physical and chemical characterizations of corn stover and poplar solids resulting from

- leading pretreatment technologies. *Bioresource Technology* 100: 3948~3962.
- Li, B.Z., Balan, V., Yuan, Y.J., Dale, B.E. 2010. Process optimization to convert forage and sweet sorghum bagasse to ethanol based on ammonia fiber expansion (AFEX) pretreatment. *Bioresource Technology* 101: 1285~1292.
- Majewicz, T.G., Padlas, T.T. 1979. Cellulose acetate and triacetate fiber. In: Grayson M, Eckroth D (eds) *Kirk-Othmer encyclopedia of chemical technology*, 3rd edn. Wiley, New York, pp. 89~117.
- Schaller, J., Meister, F., Schulze, T. Krieg, M. 2013. Novel absorbing fibres based on cellulose acetate. *Lenzinger Berichte* 91: 77~83.
- Shaikh, H.M., Pandare, K.V., Nair, G., Varma, A.J. 2009. Utilization of sugarcane bagasse cellulose for producing cellulose acetates: Novel use of residual hemicellulose as plasticizer. *Carbohydrate Polymers* 76(1): 23~29.
- Ueda, T., Onozawa, S., Akiyama, M., Sakuta, M. 1988. The influence of growth temperature and thermal annealing on the stress in GaAs layers grown on Si substrates. *Japanese Journal of Applied Physics* 27(10): 1815~1818.
- Van de Vyver, S., Geboers, J., Jacobs, P.A., Sels, B.F. 2011. Recent advances in the catalytic conversion of cellulose. *ChemCatChem* 3: 82~94.
- Voiges, K., Adden, R., Rinken, M., Mischnick, P. 2012. Critical reinvestigation of the alditol acetate method for analysis of substituent distribution in methyl cellulose. *Cellulose* 19: 993~1004.
- Vu, T.H.M., Pakkanen, H., Alén, R. 2004. Delignification of bamboo (*Bambusa procera*)-Part I. Kraft pulping and the subsequent oxygen delignification to pulp with a low kappa number. *Industrial Crops and Products* 19: 49~57.