

Complete Dissolution of Ball-Milled Masson Pine Using an Aqueous Sodium Hydroxide Solvent

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An inorganic sodium hydroxide aqueous solution was developed for the dissolution of ball-milled softwood. Extractive-free Masson pine powder was prepared from the wood meal by planetary ball milling for various lengths of time. The effects of ball milling on the dissolution and regeneration of Masson pine powder were investigated. After 4 h of ball milling, the wood powder was completely dissolved in 6 wt% NaOH aqueous solution under vigorous magnetic stirring for 10 to 20 min at room temperature. The alkaline nitrobenzene oxidation products yield of 4 h ball-milled wood was very close to that of coarse wood meal without ball milling. Regeneration of the lignin fraction was easier than cellulose during the acid neutralization process, and the dialysis regeneration yield of total biomass was 91.1%. Therefore, the complete dissolution of the Masson pine in sodium hydroxide solution is of great potential for enhancing lignin isolation with a very little structural change.

Keywords: Masson pine; Sodium hydroxide aqueous solution; Ball milling; Dissolution; Regeneration

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INTRODUCTION

The main components of lignocellulosic biomasses are cellulose, hemicellulose, and lignin. Cellulose, as a linear polysaccharide, has highly developed hydrogen bond networks and a partially crystalline structure (Yang *et al.* 2011). The lignin, derived primarily from p-hydroxycinnamyl alcohols, consists of a three-dimensional network of coupled monomers of a varied 4-hydroxyphenylpropanoid type (Fasching *et al.* 2008). Unlike most natural polymers, lignin binds with polysaccharides to form a tight chemical structure through molecular associations and covalent bonds (Chang *et al.* 1975; Lee *et al.* 1981; Ikeda *et al.* 2002). Therefore, it is difficult to dissolve native lignocelluloses completely in traditional solutions.

Complete dissolution of lignocellulosic biomass is of great importance for both efficient isolation and optimum use of the cell wall components. There are many approaches for dissolving lignocelluloses in organic or inorganic solvent systems. These solvent systems, such as N-methylmorpholine-N-oxide (NMMO) (Fink *et al.* 2001), lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) (McCormick *et al.* 1985), and ionic liquid (Kosan *et al.* 2008), have been successfully applied to dissolve cellulose. However, most of these solvent systems cannot completely dissolve lignin in lignocellulosic materials. For example, Sjöholm *et al.* (1997) and Yanagisawa *et al.* (2005) reported that softwood kraft pulps were not completely dissolved in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc). Lu and Ralph (2003) succeeded in dissolving ball-milled wood in dimethyl sulfoxide and N-methylimidazole (DMSO/NMI) at room temperature for several hours. Wang *et al.* (2009) and Gu *et al.* (2015) reported that wood

or straw samples milled in a planetary ball mill for 2 h could be completely dissolved in lithium chloride/dimethyl sulfoxide (LiCl/DMSO). Moderate ball milling is often necessary for the complete dissolution of lignocellulosic materials without delignification (Lee *et al.* 1981; Fujimoto *et al.* 2005; Holtman *et al.* 2007; Wang *et al.* 2009). However, the solvent systems suffer from serious environmental problems, difficult recycling, and high cost. Thus, an environmentally friendly solvent for complete dissolution of lignin-containing lignocellulosic materials is needed.

Recently, an aqueous sodium hydroxide solvent system with urea or thiourea was successfully developed for cotton linter dissolution at low temperature (-12 °C) (Cai *et al.* 2006, 2007). This solvent system is promising with respect to both environmental and economic issues (Jin *et al.* 2007; Qi *et al.* 2008). However, only low degree of polymerization of cellulose can be dissolved in this system (Qi *et al.* 2008). Native cellulose in lignocelluloses is difficult to dissolve in this solvent system and must be pretreated to reduce the polymer chain length (Trygg and Fardim 2011). Therefore, solvents that dissolve lignin-containing fiber materials, such as wood meal and unbleached pulps should be developed (Shi *et al.* 2014).

Masson pine (*Pinus massoniana*) is the most widespread species in the forests in southern China (Zhou *et al.* 2001). It has great potential as a raw material for a complete dissolution study. Ball milling treatment is a cost-effective and environmentally friendly physical modification method (Liu *et al.* 2011). The main purpose of this work is to develop a novel method to dissolve the ball-milled Masson pine power completely at room temperature in aqueous NaOH solution without significant structural change. The method application would widely expand the utilization of lignocelluloses as a new source for both efficient isolation and use of the cell wall components.

EXPERIMENTAL

Materials

Masson pine (*Pinus massoniana*) was collected from Sanming, Fujian Province, China, in October 2011. Air-dried chips were ground using a Wiley mill. The particles between the sizes of 40 and 80 mesh were collected and extracted with benzene-ethanol (2:1, v/v) in a Soxhlet apparatus for 12 h. The extractive-free wood meals were further dried at 40 °C overnight prior to ball milling. The ball milling was carried out with a planetary ball mill (Fritsch GMBH, Pulverisette 7 premium line, Idar-Oberstein, Germany) at 600 rpm for 0.5 h to 8 h at room temperature. The two grinding bowls were made of silicon nitride (80 mL), and each bowl contained 25 zirconium dioxide grinding balls (1 cm diameter). In each milling run, 4 g oven-dried (o.d.), extractive-free Masson pine was charged for each bowl. Each 5-min milling run was followed by a 10-min break to avoid over-heating.

N,O-bis(trimethylsilyl)acetamide (BSA) was used as silylation derivatization reagent in the analysis of nitrobenzene oxidation products and was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). All other chemicals were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., Nanjing, China.

Dissolution of Milled Wood in Sodium Hydroxide Aqueous Solution

A series of sodium hydroxide aqueous solutions with a concentration range from 2 wt% to 18 wt% was prepared. The pine powder (1% by weight) subjected to various ball

milling treatments were added to NaOH aqueous solution under vigorous magnetic stirring at room temperature.

Pine powder samples subjected to 0.5 h to 4 h of ball milling were suspended into 6 wt% NaOH aqueous solution with a concentration of 5 wt% at room temperature. After 10 to 20 min of vigorous magnetic stirring, the insoluble matter was separated and then washed with deionized water several times by centrifugation until the pH of the supernatant was 7. The washed insoluble matter was freeze-dried and weighed to calculate the dissolution ratio in NaOH aqueous solution.

Regeneration of NaOH Aqueous Solution Dissolved Masson Pine

Masson pine treated with 4 h of ball milling was completely dissolved in 6 wt% NaOH aqueous solution. Two processes, acid neutralization and dialysis regeneration, were used to regenerate the dissolved pine. For acid neutralization, the solution was adjusted to pH 0, 1, 4, or 7 using 3 M HCl and then washed three times with the corresponding hydrochloric acid solution or deionized water. For dialysis regeneration, pine dissolved in NaOH solution was poured into a seamless cellulose tube with a diameter of 28.6 mm and MWCO of 14 kDa (UC 36-32-100, EIDIA Co., Ltd., Tokyo, Japan). The sample was dialyzed in ultra-purified water at room temperature until the pH of the dialysate was 7. The regenerated solids were freeze-dried and weighed to calculate the regeneration yield. The structural components (lignin and cellulose) in dried regenerated samples were analyzed.

Analytical Methods

Klason lignin and cellulose contents were determined in the solid samples (Masson pine Wiley, milled Masson pine, and regenerated Masson pine) according to Sluiter *et al.* (2008) and Tan and Lee (2012), respectively. The yield of extractable lignin from the milled wood was determined as described in Fujimoto *et al.* (2005) and calculated as the weight percentage based on the Klason lignin content of the milled wood. The absorption coefficient of softwood lignin (15.4 L/(g·cm)) was used to calculate the extractable lignin.

Alkaline nitrobenzene oxidation (NBO) analyses were applied to the wood samples according to Chen *et al.* (1992). Nitrobenzene oxidation products were silylated with BSA at 100 °C for 10 min and then analyzed by gas chromatography under the following conditions: gas chromatograph, GC-14B with flame ionization detector (FID) (Shimadzu Co., Kyoto, Japan); column, InertCap 1 (fused-silica capillary column, 30 m, 0.25 mm i.d.) (GL Science Inc., Tokyo, Japan); column program, 5 min at 150 °C, raised by 5 °C/min to 210 °C for 0 min and by 20 °C/min to 280 °C for 6 min; injection temperature, 280 °C; detector temperature, 280 °C. Because very little p-hydroxybenzaldehyde and p-hydroxybenzoic acid were detected, the vanillin (4-hydroxy-3-methoxybenzaldehyde) and vanillic acid (4-hydroxy-3-methoxybenzoic acid) from uncondensed guaiacyl structures in lignin were the major products of nitrobenzene oxidation.

RESULTS AND DISCUSSION

Dissolution of Ball-Milled Wood in NaOH Aqueous Solution

In this work, 18 wt% NaOH aqueous solution was selected to test the solubility of the wood powder due to its strong capacity of swelling and dissolving at room temperature. The samples treated with ball milling for various amounts of time were suspended in 18

wt% NaOH aqueous solution under vigorous magnetic stirring for 10 to 20 min at room temperature. A low solid content of 1 wt% was adopted for the observation of dissolution (Fig. 1). Wood meals with short ball milling time were not completely soluble in 18 wt% NaOH. The solubility increased as the number of ball milling hours increased. The solution became clear when the ball milling time was 4 h, which indicated that the wood sample was completely dissolved.

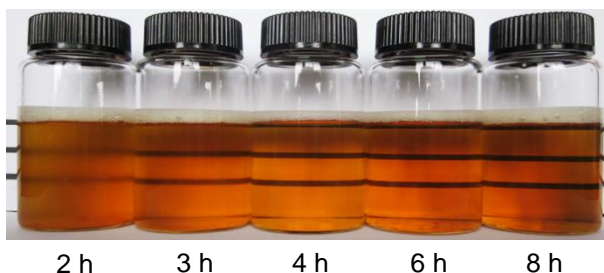


Fig. 1. The solubility of Masson pine in 18 wt% NaOH aqueous solution with various ball-milling hours

A high concentration of NaOH favors the swelling and dissolution of cellulose in lignocellulosic biomass. However, strong alkali may result in severe degradation of lignin. To minimize structural changes in lignin, the possibility of dissolving 4 h ball-milled wood in alkali aqueous solution with the NaOH concentration lower than 18 wt% was investigated. As shown in Fig. 2, only the solution of 1 wt% wood in 4 wt% NaOH aqueous solution was not very clear. Thus, 4 h ball-milled wood was completely dissolved in alkali aqueous solution with a concentration of NaOH beyond 6 wt%.

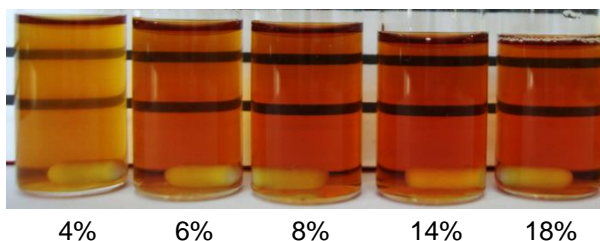


Fig. 2. The solubility of 4 h ball-milled Masson pine in various NaOH aqueous solutions

Effects of Ball Milling Hours on the Extractable Lignin and Alkaline Nitrobenzene Oxidation Products Yield

Violent milling of wood meal causes structural changes in lignin (Lee *et al.* 1981; Fujimoto *et al.* 2005; Holtman *et al.* 2007). Therefore, it is of great importance for dissolution of lignocelluloses to shorten the ball milling time without reducing final lignin yield. However, the effect of milling on the structural changes of lignin depends not only on milling time, but also on the other conditions, such as ball mill model, ball material, and operation frequency. The yields of extractable lignin under specific conditions are more useful than milling time to evaluate the milling intensity (Fujimoto *et al.* 2005).

The yields of extractable lignin and nitrobenzene oxidation products of Masson pine with various ball milling hours are given in Table 1. The extractable lignin yield increased as the ball milling time increased from 0 to 8 h. A longer ball milling time results in more cleavage of β -aryl ether bonds in lignin (Lee *et al.* 1981; Gu *et al.* 2015). However,

Wang *et al.* (2009) reported that the side-chain regions of lignin changed little when the extractable lignin yield was lower than 20 wt%. In this work, the extractable lignin yield of 4 h ball-milled Masson pine was 17.4 wt%. Therefore, although the β -aryl ether structure of lignin changes depending on the milling time, the degree of change was negligible at 4 h of ball milling time.

Table 1. Extractable Lignin Yield and Nitrobenzene Oxidation Products in Masson Pine Powder with Various Ball Milling Times

| Ball Milling Time (h) | Extractable Lignin (wt%) | NBO Products (mmol/g-KL) |
|-----------------------|--------------------------|--------------------------|
| 0 | 0.0 \pm 0.0 | 2.0 \pm 0.1 |
| 0.5 | 3.7 \pm 0.8 | 2.0 \pm 0.1 |
| 1 | 5.4 \pm 0.3 | 2.1 \pm 0.2 |
| 2 | 10.9 \pm 0.8 | 1.9 \pm 0.1 |
| 3 | 12.6 \pm 0.5 | 1.9 \pm 0.2 |
| 4 | 17.4 \pm 0.2 | 2.0 \pm 0.1 |
| 8 | 29.2 \pm 1.2 | 1.8 \pm 0.2 |

Nitrobenzene oxidation has been used extensively for studying the structural changes of aromatic moieties in lignin (Felisa *et al.* 2006). The NBO products yield of Masson pine without ball milling was 2.0 mol/g-lignin. The NBO products yield changed little when the ball milling time was lower than 4 h, and it was as high as 1.8 mmol/g-lignin when the milling time extended to 8 h. This result showed that the aromatic structures in lignin were not obviously changed under the milling conditions.

The Dissolution of Structural Components of Ball-Milled Masson Pine in NaOH Solution

As mentioned earlier, 4 h ball-milled pine was completely dissolved in 6 wt% NaOH aqueous solution at room temperature. As the ball milling time significantly affects the dissolution of the lignocellulosic materials (Lee *et al.* 1981; Holtman *et al.* 2007; Wang *et al.* 2009), the dissolution rate of the structural components of Masson pine with various ball milling times in 6 wt% NaOH aqueous solution was investigated (Fig. 3). With the ball milling hours from 0 to 4 h, the dissolution ratio of total biomass in pine increased.

The ball-milled Masson pine was completely dissolved when the milling time reached 4 h. The dissolution ratio of cellulose was higher than that of lignin in the pine sample when the wood meal was milled from 0.5 to 3 h. This result indicated that cellulose in Masson pine showed better solubility than lignin in aqueous NaOH solvent. For pine without ball milling, the solubility of cellulose and lignin was almost the same. The crystal structure of cellulose was destroyed by ball milling even with a short milling time (Wang *et al.* 2009), which was important for the swelling and dissolution of cellulose. The difference between the dissolution rate of cellulose and lignin in Masson pine increased with the ball milling time from 1 to 2 h, and then the dissolution rate of cellulose become slower than that of lignin.

The cause of the difference between the dissolution rate of cellulose and lignin might be the different structural units, linked types, and distribution of cellulose and lignin in the cell wall components.

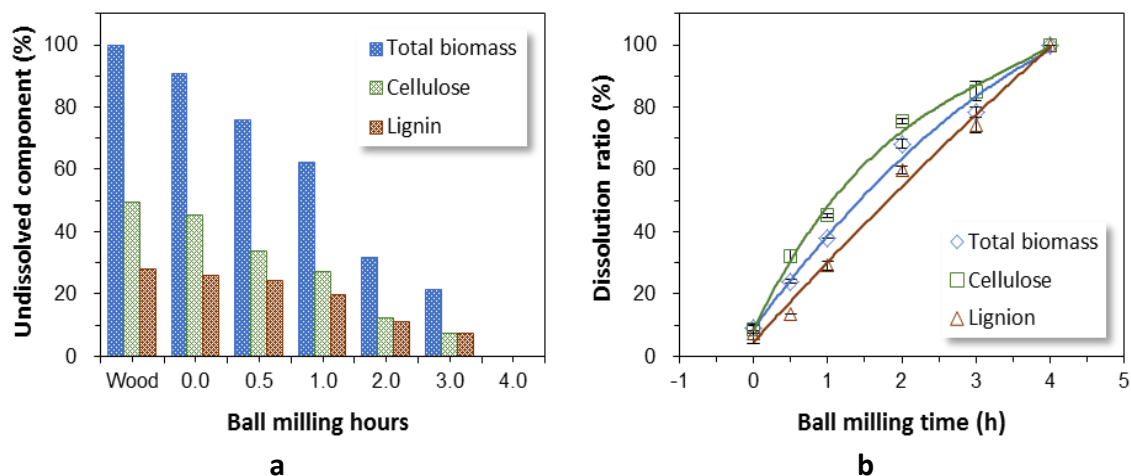


Fig. 3. The content of cellulose and lignin in undissolved residues (a) and their dissolution ratio of Masson pine with various ball milling hours in 6% (w/w) NaOH aqueous solution

Regeneration of Ball-Milled Masson Pine Dissolved in NaOH Aqueous Solution

In this work, the regeneration of ball-milled Masson pine dissolved in NaOH aqueous solution was carried out by adding HCl into the solution (Yan and Gao 2008). The pH of this solution was adjusted to 0, 1, 4, and 7 using 3 M HCl, and the regenerated lignin and cellulose were analyzed to understand the effect of pH on the regeneration of different structural components in the ball-milled pine sample.

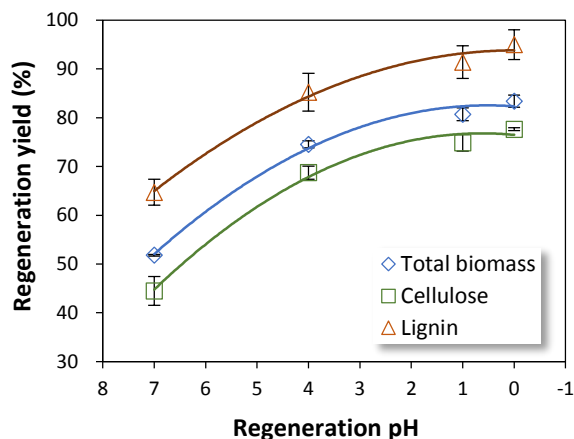


Fig. 4. The regeneration yield of 4 h ball-milled Masson pine at different pH after dissolving in 6% (w/w) NaOH aqueous solution

As shown in Fig. 4, the regenerated solid yield increased gradually as the pH was decreased from 7 to 0. The highest acid regeneration yield reached 83 wt% at pH 0, such that 17 wt% of the components in Masson pine was lost. Ball milling reduces the molecular weight of lignin and the crystallinity of cellulose (Tan *et al.* 2015). The small fractions produced in the ball milling process are difficult to recover even with regeneration under strongly acidic conditions. The regeneration ratio of lignin was higher than that of cellulose in Masson pine when the pH ranged from 7 to 0. For example, when regenerated in water at pH 7 and 0, the lignin recovery was 64.7 wt% and 95.0 wt%, respectively, but cellulose

recovery was only 44.5 wt% and 77.7 wt%, respectively. The hydrophilic property of cellulose may explain its lower regeneration yield.

The dialysis regeneration of 4 h ball-milled Masson pine dissolved in 6 wt% NaOH aqueous solution was also investigated. The regenerated solid yield of dialysis in water was 91.1 wt%, which was noticeably higher than that of the acid neutralization process (51.8 wt% at pH 7 and 83.4 wt% at pH 0). Compared to acid neutralization, more of the small fractions dissolved in aqueous alkaline solution were regenerated by dialysis.

CONCLUSIONS

1. Extractive-free Masson pine with a relatively short ball milling time (4 h at 600 rpm) was completely dissolved in 6 wt% NaOH aqueous solution in 10 to 20 min under vigorous stirring at room temperature.
2. The extractable lignin yield of Masson pine increased with the ball milling hours, and it was 17.4 wt% at the ball milling time of 4 h. In different ball milling conditions, the effects of extractable lignin yields on the alkaline nitrobenzene oxidation products yields of Masson pine were small. The cellulose component in Masson pine was easier to dissolve in the NaOH aqueous solution than lignin. The lignin fraction was easier to regenerate by acid neutralization. Compared with acid neutralization, more regenerated solids were obtained by dialysis.

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REFERENCES CITED

- Cai, J., and Zhang, L. (2006). "Unique gelation behavior of cellulose in NaOH/urea aqueous solution," *Biomacromolecules* 7, 183-189. DOI: 10.1021/bm0505585
- Cai, J., Zhang, L., Zhou, J., Qi, H., Chen, H., Kondo, T., Chen, X., and Chu, B. (2007). "Multifilament fibers based on dissolution of cellulose in NaOH/urea aqueous solution: structure and properties," *Adv. Mater.* 19, 821-825.
- Chang, H., Cowling, E., and Brown, W. (1975). "Comparative studies on cellulolytic enzyme lignin and milled lignin of sweetgum and spruce," *Holzforschung* 29(5), 153-159. DOI: 10.1515/hfsg.1975.29.5.153
- Chen, C. L. (1992). "Nitrobenzene and cupric oxidations" in: *Methods in Lignin Chemistry*, S. Y. Lin and C. W. Dence (eds.), Springer Verlag, Berlin, New York, pp. 301-321.
- Fasching, M., Schroder, P., Wollboldt, R. P., Weber, H. K., and Sixta, H. (2008). "A new and facile method for isolation of lignin from wood based on complete wood dissolution," *Holzforschung* 62(1), 15-23. DOI: 10.1515/HF.2008.003

- Felisa, D., Kien, L. N., and Adrian, F. A. (2006). "Contribution of lignin sub-structures tonitrobenzene oxidation products," *J. Wood Chem. Technol.* 15(3), 329-347. DOI: 10.1080/02773819508009514
- Fink, H. P., Weigel, P., Purz, H. J., and Ganster, J. (2001). "Structure formation of regenerated cellulose materials from NMMO solutions," *Prog. Polym. Sci.* 26, 1473-1524. DOI: 10.1016/S0079-6700(01)00025-9
- Fujimoto, A., Matsumoto, Y., Chang, H. M., and Meshitsuka, G. (2005). "Quantitative evaluation of milling effects on lignin structure during the isolation process of milled wood lignin," *J. Wood Sci.* 51, 89-91. DOI: 10.1007/s10086-004-0682-7
- Gu, F., Wu, W., Wang, Z., Yokoyama, T., Jin, Y., and Matsumoto, Y. (2015). "Effect of complete dissolution in LiCl/DMSO on the isolation and characteristics of lignin from wheat straw internode," *Ind. Crop. Prod.* 74, 703-711. DOI: 10.1016/j.indcrop.2015.06.002
- Holtman, K. M., Chang, H. M., and Kadla, J. F. (2007). "An NMR comparison of the whole lignin from milled wood, MWL, and REL dissolved by the DMSO/NMI procedure," *J. Wood Chem. Technol.* 27, 179-200. DOI: 10.1080/02773810701700828
- Ikeda, T., Holtman, K., Kadla, J., Chang, H. M., and Jameel, H. (2002). "Studies on the effect of ball milling on lignin structure using a modified DFRC method," *J. Agric. Food Chem.* 50(1), 129-135. DOI: 10.1021/jf010870f
- Jin, H., Zha, C., and Gu, L. (2007). "Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution," *Carbohydr. Res.* 342, 851-858. DOI: 10.1021/ie800833w
- Kosan, B., Michels, C., and Meister, F. (2008). "Dissolution and forming of cellulose with ionic liquids," *Cellulose* 15, 59-66. DOI: 10.1007/s10570-007-9160-x
- Lee, Z., Meshitsuka, G., Cho, N., and Nakano, J. (1981). "Characteristics of milled wood lignins isolated with different milling times," *Mokuzai Gakkaishi* 27, 671-677.
- Liu, T. Y., Ma, Y., Yu, S. F., Shi, J., and Xue, S. (2011). "The effect of ball milling treatment on structure and porosity of maize starch granule," *Innov. Food Sci. Emerg.* 12(4), 586-593. DOI: 10.1016/j.ifset.2011.06.009
- Lu, F., and Ralph, J. (2003). "Non-degradative dissolution and acetylation of ball-milled plant cell walls: High-resolution solution-state NMR," *Plant J.* 35, 535-544. DOI: 10.1046/j.1365-313X.2003.01817.x
- McCormick, C. L., Callais, P. A., and Hutchinson, B. H. (1985). "Solution studies of cellulose in lithium chloride and N, N-dimethylacetamide," *Macromolecules* 18, 2394-2401. DOI: 10.1021/ma00154a010
- Qi, H. S., Chang, C. Y., and Zhang, L. N. (2008). "Effects of temperature and molecular weight on dissolution of cellulose in NaOH/urea aqueous solution," *Cell. Chem. Technol.* 15, 779-787. DOI: 10.1007/s10570-008-9230-8
- Shi, Z. Q., Yang, Q. L., Cai, J., Kuga, S., and Matsumoto, Y. J. (2014). "Effects of lignin and hemicellulose contents on dissolution of wood pulp in aqueous NaOH/urea solution," *Cellulose* 21(3), 1205-1215. DOI: 10.1007/s10570-014-0226-2
- Sjoholm, E., Gustafsson, K., Pettersson, B., and Colmsj, O. A. (1997). "Characterization of the cellulosic residues from lithium chloride/N, N-dimethylacetamide dissolution of softwood kraft pulp," *Carbohydr. Polym.* 32, 57-63. DOI: 10.1016/S0144-8617(96)00129-4
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). *Determination of Structural Carbohydrates and Lignin in Biomass* (NREL/TP-510-42618), National Renewable Energy Laboratory, Golden, CO, USA.

- Tan, H. T., and Lee, K. T. (2012). "Understanding the impact of ionic liquid pretreatment on biomass and enzymatic hydrolysis," *Chem. Eng. J.* 183, 448-458. DOI: 10.1016/j.cej.2011.12.086
- Tan, X.Y., Zhang, B. J., Chen, L., Li, X. X., Li, L., and Xie, F. W. (2015). "Effect of planetary ball-milling on multi-scale structures and pasting properties of waxy and high-amylose corn starches," *Innov. Food Sci. Emerg.* 30, 198-207. DOI: 10.1016/j.ifset.2015.03.013
- Trygg, J., and Fardim, P. (2011). "Enhancement of cellulose dissolution in water-based solvent via ethanol-hydrochloric acid pretreatment," *Cellulose* 18, 987-994. DOI: 10.1007/s10570-011-9550-y
- Wang, Z., Yokoyama, T., Chang, H. M., and Matsumoto, Y. J. (2009). "Dissolution of beech and spruce milled woods in LiCl/DMSO," *J. Agric. Food Chem.* 57, 6167-6170. DOI: 10.1021/jf900441q
- Yan, L. F., and Gao, Z. J. (2008). "Dissolving of cellulose in PEG/NaOH aqueous solution," *Cellulose* 15(6), 789-796. DOI: 10.1007/s10570-008-9233-5
- Yanagisawa, M., Shibata, I., and Isogai, A. (2005). "SEC-MALLS analysis of softwood kraft pulp using LiCl 1, 3-dimethyl-2-imidazolidinone as an eluent," *Cellulose* 12, 151-158. DOI: 10.1007/s10570-004-0866-8
- Yang, Q. L., Qi, H. S., Lue, A., Hu, K., Cheng, G. Z., and Zhang, L. (2011). "Role of sodium zincate on cellulose dissolution in NaOH/urea aqueous solution at low temperature," *Carbohydr. Polym.* 83(3), 1185-1191. DOI: 10.1016/j.carbpol.2010.09.020
- Zhou, Z. X. (2001). *Chinese Masson Pine*, China Forestry Press, Beijing, China.

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