

PREPARATION OF XYLOSE AND KRAFT PULP FROM POPLAR BASED ON FORMIC/ACETIC ACID /WATER SYSTEM HYDROLYSIS

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A formic/acetic acid/water system was used in the ratios of 30:60:10, 20:60:20, and 30:50:20 separately for efficient hydrolysis and bioconversion of poplar chips, under the solid/liquid ratio of 1:12(g/ml), at 105 °C for 30, 45, 60, 75, and 90 min, respectively. The highest yield of 69.89% was at a formic/acetic acid /water ratio of 30:50:20(v/v/v), with solid/liquid in the ratio of 1:12(g/ml) at 105 °C for 90min. Lower kappa number and similar yield were achieved when hydrolytic residual woodchips were used for kraft pulping with over 2% Na₂O and temperature 5 °C lower compared to untreated chips. Pulps from prehydrolysis-treated chips were easy to beat. But the tensile index, tear index, and burst index of the handsheets obtained from pulp with lowest kappa number from prehydrolysis-treated poplar chips were lower than those of the pulp from the untreated chips. Considerable xylose could be obtained from the prehydrolysis stage following kraft pulping under the same conditions for prehydrolysis-treated chips and untreated chips. However, by building on the mature kraft pulping and xylitol processes, large amounts of xylose from the hemicellulose were obtained in prehydrolysis, allowing production of high-valued products via biorefinery pathways. An economical balance of chemical dosage, energy consumption, pulp properties, and xylose value for prehydrolysis with organic acid should be reached with further investigation.

Keywords: Formic/Acetic Acid /Water; Hydrolysis; Eastern Cottonwood; Poplar; Xylose; Kraft pulping

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INTRODUCTION

Bioethanol is thought to be the most promising research direction to meet the increasing demand of energy and control of environmental pollution (Wyman 1999). The exploitation of starch and saccharides for ethanol production is restricted (Qu 2007), because of the world's growing population, high cost of pretreatment, and the low conversion rate of pentose (Zhu et al. 2009; Hu et al. 2008). Thus the biochemical conversion technology from biomass to ethanol has not been industrialized yet. In another aspect, technologies for tropical *Candida* fermentation of sugars to produce ethanol, and the kraft pulping of lignocellulosic biomass have been mature for years and

widely utilized in industry. The creative combination of these two diverse technologies will enable the future development of biorefinery systems.

If a pulping procedure of lignocellulosic materials is to be applied to the biorefinery process, then the concentration of pentose after pretreatment, the characteristics of lignin, and the yield of pulp should be taken into consideration. So far, studies of various pretreatment methods such as hot water/steam-explosion, alkaline, dilute acid, and organic solvent have been developing rapidly (Mosier et al. 2005; Pan et al. 2005). However, the concentration of pentose resulting from hot water pretreatment has been too low, and the strength of paper obtained from the subsequent pulping of residue is adversely affected (Sung et al. 2008; Sung and von Heiningen 2008). Though the concentration of pentose from hydrolysis of lignocellulosic materials with dilute acid (for example, sulphuric acid, hydrochloric acid, and phosphoric acid) pretreatment was higher, the toxicity, causticity of the solution used for digestion, and damage to the cellulose crystal structure have increased the cost of the sequent fermentation process (Kumar et al. 2009). As for alkaline agents such as NaOH, Ca(OH)₂, and Mg(OH)₂, pretreatment that has a favorable effect of swelling, activating, and removing lignin to the extent also has the disadvantage of being time-consuming, and there is a high degree polymerization of pentose and high content of residual lignin in the hydrolyzed material. Regarding organic solvent pretreatment, an appropriate content of pentose can be obtained, and the cellulose can be well protected; however, the negative effects following organic solvent pretreatment are its high recycling cost and strong inhibiting effect on the microorganisms used in fermentation. Formic acid and acetic acid, due to their good catalytic capability, ability to dissolve lignin (Xu 2006), low boiling point, and easy recycling (Sun and Cheng 2002; Rousu et al. 2001), are considered to be good solvents for pretreatment for lignocellulosic materials.

Hence, in order to improve the system's hydrolyzing ability and inhibit the condensation of lignin, a formic acid/acetic acid/water system to pre-extract poplar chips was utilized in this experiment so as to explore a new path for highly efficient pretreatment of cellulosic materials to produce ethanol.

EXPERIMENTAL

Materials

Eastern cottonwood (*Populus deltoides*, commonly known as "poplar") chips were kindly supplied by Tiger Forest & Paper Group Co. Ltd, China. The components composition of the wood (% w/w) was cellulose 44.49%, hemicelluloses 19.36%, Klason lignin 22.38%, and acid soluble lignin 1.41%. The wood was cut into chips with the dimensions of 30mm x 5mm x (2-3)mm, dried in air, and stored at room temperature. Chemically pure formic acid and acetic acid were purchased from Fluka Co.

Methods

Formic acid/acetic acid hydrolysis

Hydrolysis was carried out in a 500 ml glass reactor at atmospheric pressure. Chips (20.0g) after phenol-ethanol (9:1) extraction were treated with formic acid/acetic

acid/H₂O (20/60/20, 30/60/10, 30/50/20, v/v/v), at 105°C for 30, 45, 60, 75, and 90 min with a ratio of liquor to solids 12:1 (ml/g), respectively. After filtration for separation of solid and liquids, the resulting hydrolysates were concentrated in a 1L evaporator at 75°C under vacuum in order to extract reactants of formic acid and acetic acid from the reaction solution. Subsequently, the hydrolysates were detoxified with CaCO₃ by neutralizing the pH to 5.0, removing these compounds, which are possibly toxic to the microbial metabolism during consequential fermentation. The filtered solid residues were rich in cellulose and were washed with water until the pH was adjusted to 5.0, then dried at 60 °C for 16 h. The reducing sugar concentrations were spectrophotometrically determined according to the method by Deng and Tabatabai (2002) using dansyl amino acids at 260 nm in a UV-745GD spectrophotometer (Analytical Co., Shanghai, China). Each experiment was carried out in triplicate under identical conditions to get the mean value. Xylose concentrations were measured by high pressure liquid chromatography (HPLC) (Waters, Milford, USA) with a Waters Sugar Pak I column (Waters, Milford, USA) and a refractive index detector (410 Series, Waters, Milford, USA). According to the procedure of Sun (2002), during the measurement, samples were previously filtered through a 0.45µm filter and injected in the chromatograph under the following conditions: injection volume of 10µL, column temperature of 90°C, and high purity water as the mobile phase, used at a flow rate of 1.1mL/min. All experiments were performed at least in duplicate. Yields and concentrations of the xylose are given on the dry weight basis of the starting material.

Morphological properties and chemical composition analysis of poplar woodchips

In order to discover the morphological changes of the woodchips after treatment with organic acid, the chips with the prehydrolysis treatment were measured with a KAJAANI FS-200 fiber automatic analyser and microscope (Wu et al. 2007). Poplar chips prior to hydrolysis treatment were also measured for comparison.

The cold and hot-water (T207 om-99), 1%NaOH (T212 om-98), benzene-alcohol (T204 om-88) extractions, Klason and acid soluble lignin (T222 om-98) measurements, cellulose (Browning 1967), and pentosan (T223 cm84) quantification were carried out with TAPPI Test Methods, respectively.

Kraft pulping and properties of pulps

The kraft pulping process was performed in a CAS 420 oil bath digester. The untreated chips were cooked under the following conditions: active alkali charges of 10%, 12%, 14%, 16%, and 18% (as Na₂O); 22% sulfidity; a liquor-to-wood ratio of 4.5:1; a cooking temperature of 165 °C; and retention times of 90 min, 120 min, and 150 min, respectively. The cooking conditions for prehydrolysis-treated chips were: active alkali charges of 12%, 14%, 16%, and 18% (as Na₂O); sulfidity of 22%; a liquor-to-wood ratio of 4.5:1; cooking temperatures of 155 °C, 160 °C, 165 °C, and 170 °C; and retention times of 60 min, 90 min, 120 min, and 150 min, respectively. Scale-up pulp experiments were carried out in a 10 L pulp digester (M/K609-2-10).

Pulp was washed with tap water until all chemicals were removed. The yield of the pulp was determined gravimetrically from the oven-dried weight of the poplar wood. The kappa number and viscosity were determined according to T236 om-85 and SCAN-

CM 15:88 standard methods. The determinations of hexeneuronic acid groups in chemical pulps were according to reference of Cheng (2007). The pulp was beaten in a PFI mill. The handsheets of about 60g/m² were made in a Rapid Kothen Sheet Making Machine. The sheets were tested for tensile (T494 om-96), tear (T414 om-98), and burst (T403 om-97), according to the TAPPI Standard Test Methods, respectively.

RESULTS AND DISCUSSION

Yield and Concentration of Xylose Obtained from Prehydrolysis Stage

Acetic acid and formic acid can be employed to delignify lignocellulosic materials. The results showed that they are capable of diffusing through the surface layer of lignocellulosic fiber, dissolving the lignin, breaking down the bonds in hemicellulosic molecules, and decomposing polysaccharides into monosaccharides. Yield and concentration of xylose from hydrolysis of formic acid / acetic acid system are shown in Fig 1. Treatment of the poplar chips with formic acid/acetic acid/H₂O (30/60/10, v/v/v), formic acid/acetic acid/H₂O (30/50/20, v/v/v), and formic acid/acetic acid/H₂O (20/60/20, v/v/v) at 105 °C for 30 min released 1.85, 1.74, and 1.75 g/L xylose, respectively. When hydrolysis time was increased from 30 to 90 min, the xylose yield in formic acid/acetic acid/H₂O (30/60/10, v/v/v) system increased from 40.13% to 68.53%, and the concentration was up to 2.30 g/L. So did the other two systems; the yields reached to 60.30% and 69.89%, and the concentrations were 2.19 g/L and 2.37 g/L at the end of the hydrolysis, respectively.

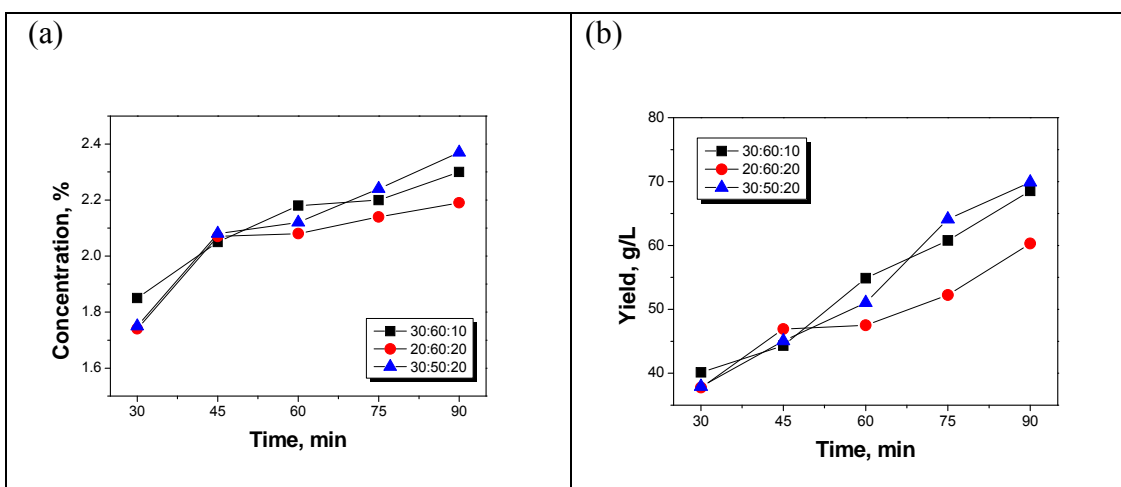


Fig. 1. Effect of three combinations of amounts of a formic/acetic acid/water system on the concentration and yield of the release of poplar xylose; (a) Xylose concentration vs. time; (b) Yield* vs. time.

* Yield of release of xylose from poplar = (Concentration of xylose in hydrolyzate/total reducing sugar concentration in hydrolyzate) x100%

Effect of Hydrolysis Time on Yield and Concentration of Xylose

From Fig. 1, the rates of yield and concentration increase of xylose before hydrolyzing 45 min were greater than after the prehydrolysis stage. This phenomenon may be related to the composition and structure of the raw material. In the surface of poplar chips, 22.38% of insoluble lignin and 48.29% of cellulose were found, and they are compact in structure. Moreover, the structure of cellulose is possibly unbreakable under the temperature of 105 °C. A certain amount of organic acid is consumed to permeate to the interior structure of chips. These two indexes reached to a peak after hydrolysis for 90 min, as shown in Fig. 1. This can be explained by the decomposition of hemicellulose. As some literature has reported (Carvalho 2005), hemicellulose can be broken down into monosaccharides, such as xylose, galactose, and glucose. Some of these may be hydrolyzed further into acetic acid, furfural, and furan in the acidic condition (Cheng 2007). The newly formed acetic acid partly remains in the hydrolyzing solution with chips and continues to have a significant effect on hydrolysis of hemicellulose with formic acid.

Effect of Organic Acid on Yield and Concentration of Xylose

It was found that the rate of hydrolysis in the formic/acetic acid /water 30:50:20(v/v/v) system was the fastest during the initial 45 min. At the end of 45 min, the yield and concentration of xylose were 46.93% and 2.05g/L, respectively. However, after that period, the rate of hydrolysis slowed down. The yield and concentration of xylose were lower than in the other two systems. The main difference between it and the other systems was the ratio of formic acid. As analyzed, the beginning 45 min could be defined as a penetration process. The change in the ratio of formic acid from 20% to 30% appears to have made no evident effect on this process. That means that the dominant variety of acids that penetrated into the inner structure of chips was acetic acid rather than formic acid. However, when organic acid did not get into the inner structure of the chips, the effect of formic acid on yield and concentration of xylose were evident. This could be explained by its structure. Sun et al. (2007) stated that in the crystal structure of cellulose there is an area of $0.238 \times 0.279 \times 0.240$ nm, which is enclosed by the O6•••O2 bonds of one chain (or molecular), and O3•••O5 bonds of another chain (or molecule) for formic acid to go in. Once the formic acid penetrates into the crystal lattice, the crystalline lattice of cellulose can swell. Eventually, the rigid framework of the crystalline lattice of cellulose is broken open.

Effect of Organic Acid Treatment of Poplar Chips on Fiber Morphological Properties and Chips Chemical Composition

The morphological properties and chemical compositions of poplar chips before and after prehydrolysis-treatment are shown in Table 1 and 2. On the basis of morphological properties and chemical compositions, prehydrolysis-treated and untreated woodchips could be pulped; however, a modified pulping process for prehydrolysis-treated woodchips is expected. From Table 1, fiber length and width were decreased from 0.894mm to 0.827mm, and from 20.48 μ m to 20.24 μ m after treatment with organic acid. And when treated with organic acid, length-width ratio also declined from 43.65 to 40.86, the other morphological properties were almost unchanged. After treatment with organic

acid, extractives of the woodchips responding to 1% NaOH and benzene-alcohol treatment were decreased in extent from 18.23% to 11.20% and from 1.47% to 0.82%, respectively. Klason lignin, acid soluble lignin, and pentose also were dissolved out of the chips, bringing down their contents in the chips separately from 22.38% to 18.17%, from 1.41% to 0.80%, and from 19.36% to 10.87%. 36.02% of the lignin and 54.95% of the hemicellulose was removed from the woodchips in the pre-hydrolysis stage. Therefore, the pre-hydrolysis may be regarded as a first-step pulping stage, involving a mild pulping condition.

Table 1. The Morphological Changes of Poplar Chips

| | Length (mm) | Width (μm) | Fiber wall thickness (μm) | Lumen diameter (μm) | length-width ratio | Ratio of cavity to width | Ratio of wall to cavity |
|-----------------------|-------------|-------------------------|--|----------------------------------|--------------------|--------------------------|-------------------------|
| Untreated | 0.894 | 20.48 | 2.83 | 9.27 | 43.65 | 0.45 | 0.61 |
| Prehydrolysis-treated | 0.827 | 20.24 | 2.84 | 9.31 | 40.86 | 0.46 | 0.61 |

Table 2. The Chemical Composition Changes of Poplar Chips

| | Extraction (%) | | | | Klason lignin (%) | Acid soluble lignin (%) | Cellulose (%) | Pentose (%) |
|-----------------------|----------------|------------|---------|-----------------|-------------------|-------------------------|---------------|-------------|
| | Hot water | Cold water | 1% NaOH | Benzene-alcohol | | | | |
| Untreated | 3.57 | 0.33 | 18.23 | 1.47 | 22.38 | 1.41 | 44.49 | 19.36 |
| Prehydrolysis-treated | 5.01 | 0.44 | 11.20 | 0.82 | 18.17 | 0.80 | 56.87 | 10.87 |

Kraft Pulping

In order to discover the effects of organic acid pre-treatment on kraft pulping, the pulping conditions of both untreated and prehydrolysis-treated chips were examined. Kappa number and yield during the pulping condition are shown in Fig. 2. Variation of pulp's yield with kappa number was found under different pulping conditions. From Fig. 2 (a) and (c), it can be observed that the yield of pulps decreased exponentially with the decline of kappa number in the given initial concentration of cooking active alkali. Moreover, it can be seen that the yield of untreated chips pulp dropped faster when the kappa number was below 16-17, and so did that of prehydrolysis-treated chips pulp when the kappa number was below 14-15, providing evidence that kappa numbers of 16-17 and 14-15 were the turning points of pulping for the two kinds of chips, respectively. The lower were these points of kappa number separately, the higher were the yields of pulps that were obtained.

The yield of unbleached pulp, which is called apparent yield, is composed of cellulose, hemicellulose, and residual lignin. The purpose of chemical pulping is to remove lignin. In order to evaluate the pulping process preferably, it is better to eliminate the yield that is contributed by the residual lignin. As introduced, the kappa number of

the KP pulp is mainly affected by the residual lignin and HexA (Chai et al. 2001). The percentage of residual lignin could be calculated from the following formula,

$$L = 0.13 \times (K - 0.086 * HexA) \quad (1)$$

where L is the percentage of residual lignin, and K and $HexA$ are the kappa number and the content ($\mu\text{mol/g}$) of HexA. The value 0.13 is the proportionality coefficient of kappa number and the content of lignin ($L=0.13 \times \text{kappa number}$, when the yield of pulp is below 70%) (TAPPI 1996). The value 0.086 is the proportionality coefficient that HexA gave to the measured kappa number (10 μmol HexA is equated with 0.84-0.86 unit of kappa number) (Li and Gellerstedt 1997). Therefore, the yield without the contribution of lignin (Y_l) could be calculated as follows:

$$Y_l = Y - 0.13 \times (K - 0.086 * HexA) \quad (2)$$

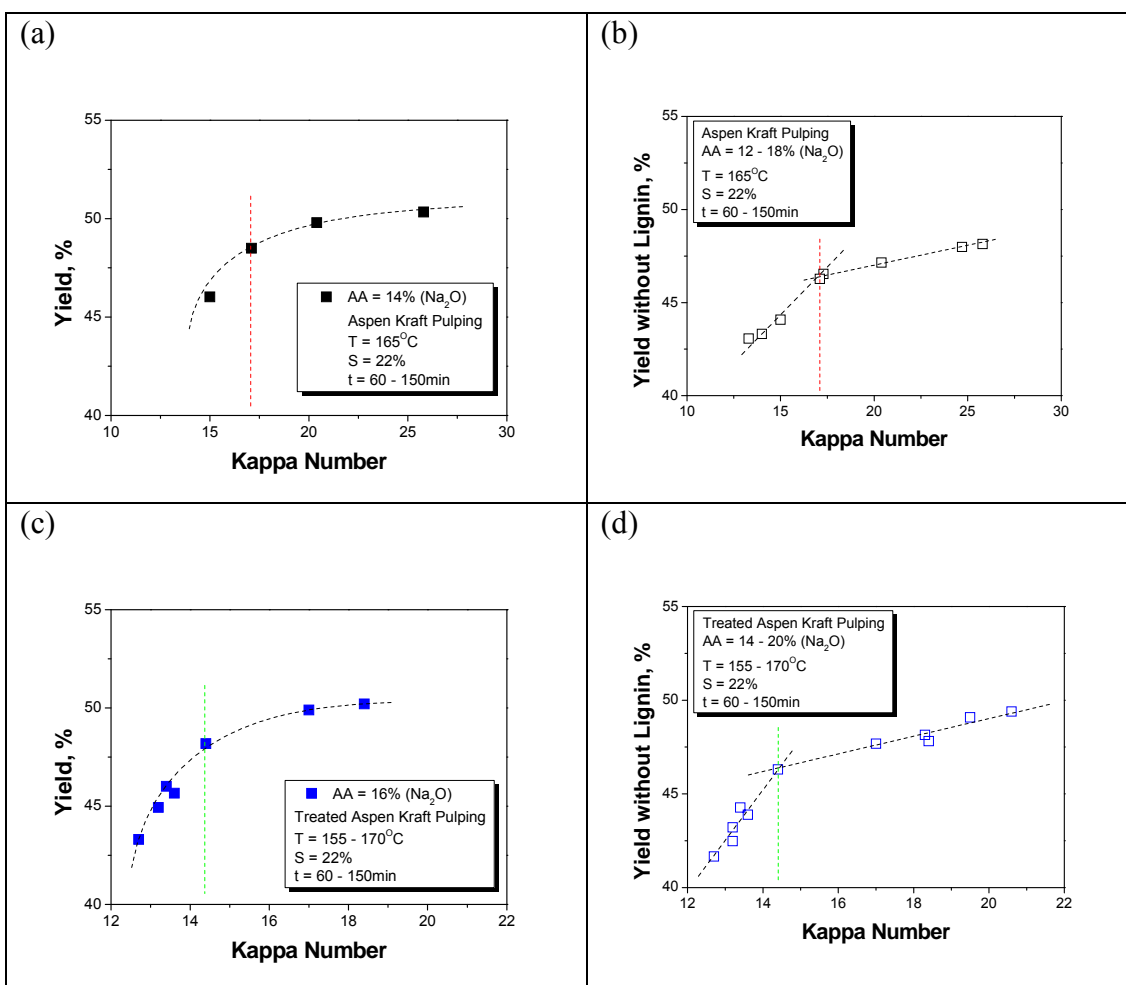


Fig. 2. The yield of pulp at different kappa number

Figure 2 (parts b and d) shows the relationship between the yield without the contribution of lignin (Y_t) and kappa number. For both untreated and prehydrolysis-treated chips, though pulping condition varied, a good linear relationship was kept between these two varieties of chips when $Y_t < 46.3\%$ ($Y = 48.5\%$) and $Y_t < 46.3\%$ ($Y = 48.2\%$). Comparing the change regularity of kappa number, the cellulose and hemicellulose would be degraded more quickly when the Y_t values were below 46.3% and 46.2%, respectively, as the pulping process continued. It can be shown from Fig. 2 (a) and (c) that the characteristic yield ($Y \approx 48.5\%$, and $Y \approx 48.2\%$) were obtained when the kappa numbers were in the range of 16-17 and 14-15 at the beginning concentrations of active alkali of 14% and 16% separately, with their factors H of 1294 and 848.

In comparison with these two factor H s, it was found that the lignin in prehydrolysis-treated chips was more easily removable due to the pretreatment that could destroy the intensive structure of woodchips, leading to substantial degradation of hemicellulose, although more alkali was consumed during pulping of chips after prehydrolysis. At the same time, the yield of pulps from chips with and without pretreatment was not completely different. Perhaps the hemicellulose from untreated woodchips would be degraded unavoidably when a large amount of lignin was removed to a certain extent in the process of pulping.

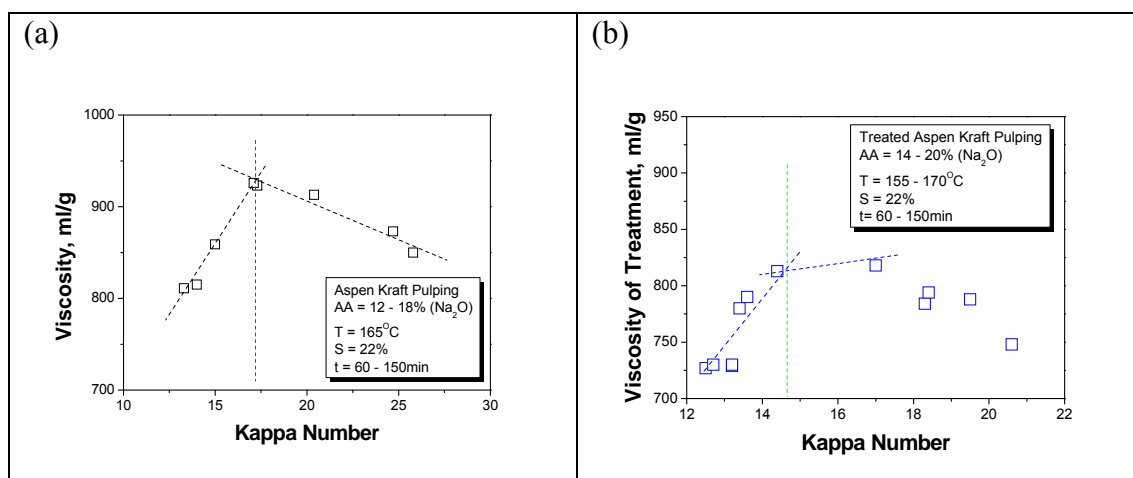


Fig. 3. The viscosity of pulp at different kappa number

Pulp's viscosity and strength, which indicate the extent of damage of cellulose and hemicellulose during pulping, are directly related. In a strict sense, the recent methods of measurement for the viscosity of unbleached pulp, which contains a high amount of lignin, are not suitable. The reason is that the lignin may affect the rheology of cellulose in the solution of copper ethylene diamine, which could lead to the value measured being far below the real value. From Fig. 3 (a) and (b), it can be seen that the viscosity did not reach the peak until the kappa number was 16-17. When the kappa number is below 16, the lower content of lignin cannot have a significant effect on the rheology of cellulose in copper ethylene diamine solution. Instead, the degradation of cellulose may affect the viscosities, inducing its obvious decline. From Fig. 3 it can be seen that the inflexion of viscosity for pulps from chips with and without prehydrolysis

treatment was at the kappa numbers of 14-15 and 16-17. However, the viscosity of untreated pulp is much higher than that of prehydrolysis-treated pulp, possibly because of the destruction of cellulose crystallization, just as that caused by the organic acid pretreatment (Xu et al. 2006).

Physical Properties of Handsheets from Unbleached Pulps

The tensile index, tear index, and burst index were tested for handsheets in this experiment. The results are shown in Table 3. It can be seen that approximately the same beating degree of 47°SR was obtained from pulps from the organic acid-treated poplar woodchips when beating level at 500 revolutions was applied, it was less than that of the pulp from the untreated chips, indicating that pulps from prehydrolysis-treated woodchips were easy to beat for further papermaking. However, the tensile index, tear index, and burst index of the handsheets obtained from pulps of prehydrolysis-treated chips were 40.03 N•m/g, 3.38 mN•m²/g and 3.15 kPa•m²/g lower than those of the pulps from the untreated chips. Therefore, weaker physical properties of pulps from the prehydrolysis-treated poplar chips were observed in comparison with those of the untreated chips.

Table 3. Physical Properties of Handsheets from Unbleached Pulps

| | Rotation speed of beating (rpm) | Beating degree (°SR) | Gram., (g.m ⁻²) | Tensile (N•m/g) | Tear index (mN.m ² /g) | Burst index (kPa.m ² /g) |
|-----------------------|---------------------------------|----------------------|-----------------------------|-----------------|-----------------------------------|-------------------------------------|
| Untreated | 6500 | 48 | 58.1 | 92.143 | 8.72 | 7.47 |
| Prehydrolysis-treated | 5000 | 46.5 | 59.4 | 52.112 | 5.34 | 3.32 |

CONCLUSIONS

1. The degradation of xylose was found to increase when more intensive conditions of reaction time and temperature were employed. The optimum yield of xylose was 69.89% with the concentration of 2.37g/L in the reaction system of formic/acetic acid /water. Moreover, fiber morphological properties and chemical composition of poplar woodchips were partially destroyed in the case of prehydrolysis-treated samples. However, lower lignin, lower content of hemicellulose, and higher content of cellulose were obtained in the pulp from prehydrolysis-treated woodchips, following a lower Kappa number and similar yield of the pulp from untreated woodchips when active alkali charge of 16% (as Na₂O) was applied with sulfidity of 22% and the liquor-to-wood ratio of 4.5:1.
2. Higher chemical charges were required for the pulping of the prehydrolysis-treated woodchips, partly due to an obvious amount of the residual acid remaining in the prehydrolysis-treated chips. Moreover, the tensile index, tear index, and burst index of pulps obtained from prehydrolysis-treated poplar chips were 40.03 N•m/g, 3.38 mN•m²/g and 3.15 kPa•m²/g, which was distinctly lower than those from untreated chips. Therefore, compared to that from the untreated poplar chips, the more

preferable physical properties of pulps were expected to improve from prehydrolysis-treated poplar chips.

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