New Technologies in Non-wood Fiber Pulping and Papermaking

5th INWFPPC, Guangzhou, China, 2006

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Preface

Paper industry is a mainstay industry and was recognized as an inexhaustible promising industry. It provides us commercial material for packing, printing, publishing and information industries, can leads development of forestry, machinery and chemical engineering etc. In China, paper has been produced from non-wood fibrous raw materials since Han Dynasty. Up till now, China still produces largest amount of paper from non-wood fiber.

The China Technical Association of Paper Industry hosted the 1988 International Non-Wood Fiber Pulping and Papermaking Conference in Beijing. After that the conference was successfully held in Shanghai, Beijing and Jinan in 1992, 1996 and 2000 respectively. This indicates that both the enterprises and technicians attach importance of papermaking from non-wood fibers.

It's our honor to organize the 5th International Non-Wood Fiber Pulping and Papermaking Conference at South China University of Technology. The State Key Laboratory of Pulp and Paper Industry has been applying itself on the fiber chemistry, pulping, bleaching and papermaking from non-wood fibrous raw materials since its establishment. A great number of achievements have been made. The conference provides us an opportunity to communicate the latest achievements in non-wood fiber pulping and papermaking. A total of 94 papers have been accepted after the review by the committee members. We believe that the academic exchange will favor the advance of the technology of papermaking.

We would like to express our thanks to the National Natural Science Foundation of China for financial support. We are also thankful to China Technical Association of Paper Industry and South China University of Technology for their support. The support from the members of program committee and organization committee is also appreciated.

Zhan Huaiyu, Chen Fangeng and Fu Shiyu
South China University of Technology

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Session 3 Advances in Nonwood Fiber Pulping, Chemimechanical Pulping and Pulp Bleaching

Session 6 Biotechnology in Nonwood Fiber Processing

CORNSTALK AS A SOURCE OF FIBER AND ENERGY

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ABSTRACT

Cornstalk, among the agricultural residues and other non-wood fiber, is the most promising source of fiber in the countries where there is a lack of forest resource such as in China and India. However, the usage of cornstalks is very limited in pulp and paper industry. Cornstalk contains about 27% hemicelluloses, which is higher than most of the hardwoods and other non-wood fiber materials. Preservation of hemicelluloses in papermaking fiber is important for increased fiber-to-fiber bonding and pulp yield. Unfortunately, in conventional pulping process, most of the hemicelluloses are degraded and ends up in pulping liquor. The calorific value of hemicelluloses derivatives in black liquor is very low compare to lignin derivatives. A value added alternative is to partially extract hemicellulose in cornstalk prior to pulping by dilute acid hydrolysis in the form of sugar suitable for fermentation into ethanol without reducing fiber quality. Dilute acid hydrolysis process under various conditions has been applied for partial removal of hemicelluloses. The residual materials were pulped using soda-AQ process. The separation of hemicelluloses is optimized to protect the paper strength properties.

Keywords: nonwood fiber, cornstalk, pulp

INTRODUCTION

Recent price hike of petroleum in the world market has given economic incentive to convert renewable lignocellulosic materials into energy. Two stages of acid hydrolysis were suggested to convert the hydrolyte fraction of hardwood into fermentable sugar for the production of ethanol [1,2]. Indeed, several Companies and research institution are in the process of producing ethanol from fermentation of sugar derived from biomass through acid hydrolysis and/or enzymatic hydrolysis [3]. In this process, biomass needs to be grounded into small particles to enhance the acidic or enzymatic hydrolysis, which is very energy intensive especially for woody biomass.

In traditional chemical pulping process, most of the lignin, hemicelluloses and part of celluloses are degraded and ended up in black liquor that produces energy through combustion. However, the contribution of hemicelluloses and celluloses derivatives in black liquor in energy conversion is very low compared to those of lignin derivatives. Attempts were taken previously to separate hemicelluloses from wood chips by hydrolysis before proceeding for pulping. In those cases, objectives were to produce rayon grade viscose pulp. Prehydrolysis products were not further processed [4,5]. Recent concept of value prior to processing biorefining [6,7], in which hydrolyzed materials are used for ethanol production through fermentation and solid residues for pulp production, has drawn much attention of scientific community.

Agricultural residues such as cornstalk offer a promising alternative to hardwood and softwood species in terms of fiber as well as energy under value prior to processing concept. Cornstalk contains more hemicelluloses than wood that can be partially extracted prior to pulping without reducing pulp and paper quality. The hemicelluloses in the form of fermentable sugar were extracted to produce ethanol. The average fiber length of cornstalk pulp is similar or better than hardwood pulp. The characteristics of fiber and pulping processes for softwood and hardwood compare to cornstalk are shown in Table 1. In fact, cornstalk pulp can serve as an important raw material for printing, writing and specialty grades paper[8]. Many developing countries, where the forest resources are limited, have turned to non-wood plants and agro-based materials for papermaking [9]. Currently, the use of agricultural residues for pulp and papermaking in the United States is negligible, although nearly 284 million tons including 150 million tons of cornstalk are annually available [10]. The objective of this study is to demonstrate this value prior to processing concept using cornstalk for simultaneous production of fermentable sugar and pulp in laboratory. The study is focused on sugar and pulp yields and pulp quality under various hydrolysis and pulping conditions.

Table 1 Fiber characteristics and pulping processes for wood and cornstalk materials (9-13)

Fiber source	Average fiber length (mm)	Fiber size diameter (μ m)	Cellulose (%)	Lignin (%)	Pentosans (%)	Pulping process
Softwood	2.7~4.6	32~43	40~52	26~32	8~12	All
Hardwood	0.7~1.6	20~40	38~50	18~28	15~25	All
Cornstalk	1.0~1.5	18~22	46~50	16~17	27~28	Soda, Kraft

EXPERIMENTAL

Materials

Cornstalk was procured from a farm near Madison in Wisconsin, USA. The cornstalk used in this project was standing in the field throughout the winter and harvested in April. Insect or mold did not deteriorate the cornstalk quality. The humidity level of cornstalk was less than 20% during harvesting. Cornstalk stems were separated manually from the leaves and other unwanted materials. Based on our previous observation, the bottom 3 to 4 ft of cornstalk is the best source of quality fiber[8]. Separating the pith from this part is not necessary, since the pith content is relatively low and substantial amount of good quality fibers are present. Cornstalk stems were cut into pieces varying from 2 to 4 cm long and dried in air to a humidity level of 8%.

Hydrolysis and pulping

Dilute sulfuric acid of concentration 0.25%, 0.5% and 1% based on oven dry cornstalk was used in prehydrolysis while maintaining the liquor to cornstalk ratio 4:1. The hydrolysis temperature was Varied from 120℃ to 140℃ for a period varied from 15 min to 60 min and a ramp time of 30 min. Cornstalk residues after dilute acid hydrolysis were pulped at 150℃ for a period varying from 15 to 30 min using liquor with 12% active alkalinity and 0.5% AQ except sample CSP-6 where AQ was not included in the liquor. Cornstalk without prehydrolysis was pulped at 160℃ for 60 min using liquor containing 12% active alkalinity and 0.5% AQ as control for comparison purposes (sample CSP-4). Sugar analysis of cornstalk and liquid fraction of hydrolysis was carried out by the Analytical Chemistry and Microscopy Laboratory of USDA Forest Products Laboratory (Madison, WI, USA). Handsheets preparation and paper testing were done following the TAPPI methods.

RESULTS AND DISCUSSION

Data in Table 2 lists the results of sugar analysis of the cornstalk sample used in this study. The total carbohydrate in the form of sugar obtained from the sample was 55.6%. The remaining fractions are lignin, extractives and unaccounted.

Table 2 Sugar analysis of cornstalk

Arabinan (%)	Galactan (%)	Rhamnan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Total carbohydrate Yield(%)
1.25	0.57	0.04	38.47	15.13	0.11	55.6

Table 3 Acid hydrolysis conditions and hydrolysis products

Exp no	Acid conc. (%)	Temp. (℃)	Time (min)	Solid residue, (%) of cornstalk	Total carbohydrate (%) of cornstalk	Free Sugar (%) of cornstalk	Oligomers (%) of cornstalk	Total carbohydrate (%) of total carbohydrate in cornstalk
CS-2	0.5	120	15	90	6.86	6.14	0.72	12.34
CS-7	0.25	130	60	86	6.88	5.7	1.18	12.37
CS-12	1.0	120	30	86	4.14	2.98	1.16	7.45
CS-17	0.5	140	15	86	7.39	6.52	0.87	13.29
CS-23	0.5	130	15	88	7.37	6.08	1.29	13.26

Twenty-seven prehydrolysis experiments were carried out based on a 3 by 3-factorial design in a wide range of acid concentration, reaction temperature and duration. Some data are presented in Table 3 as an example. The yield of solid residues yield from prehydrolysis process ranges from 80% to 90%, thus excessive removal of celluloses/hemicelluloses was avoided. The objective of the prehydrolysis is to remove the cellulosic/hemicellulosic fraction of cornstalk that is easily degraded to soluble products in pulping process.

Liquid fraction of prehydrolysis products was analyzed for free sugar and the results are listed in Table 3. However, the prehydrolytic products contain both free sugars and oligomers. Table 4 lists the yields of various components of the five prehydrolysis experiments. Further acid hydrolysis of liquid fraction was done to convert all oligomers into free sugar and the results are listed in Table 5. The results (Tables 4 and 5) from the two subsequent hydrolysis processes were used to calculate the prehydrolysis yields of total carbohydrate, free sugar, and oligomers (Table 3). The total carbohydrate yields based on feed cornstalk varies from 4% to 10% for the 27 experiments conducted but only the results from 5 are listed, which is equivalent to 7 to 19% based on total carbohydrate in cornstalk.

Table 4 Sugar analysis of liquid fraction of hydrolysis process

Sample	Suc	Arab	Gal	Rham	Glc	Xyl	Man	Fruc	Total Carbohydrate
CS-2	7.288	0.549	0.100	-	23.862	0.250	-	29.228	61.277
CS-7	2.460	1.240	0.160	-	24.400	0.280	0.520	27.900	56.960
CS-12	0.560	2.140	0.120	0.040	1.200	0.360	-	25.240	29.660
CS-17	0.756	1.617	0.168	-	30.135	0.294	0.252	35.259	68.481
CS-23	0.560	2.380	0.280	-	26.120	0.520	-	30.880	60.740

Non-hydrolyzed: mg/g(OD) cornstalk as free sugar.

Table 5 Sugar analysis of hydrolyzed liquid fraction of hydrolysis process

Sample	Arab	Gal	Rham	Glc	xyl	Man	Total Carbohydrate
CS-2	1.171	0.724	-	28.554	1.473	-	31.922
CS-7	2.698	1.400	-	30.140	3.040	1.060	38.338
CS-12	3.284	1.400	-	6.560	3.640	0.700	15.584
CS-17	2.709	1.239	-	33.369	3.318	0.861	41.496
CS-23	3.871	1.640		30.620	5.040	0.940	42.111

Hydrolyzed: mg/g (OD) cornstalk as free sugar.

Table 6 Pulping conditions of hydrolyzed and non-hydrolyzed (CSP-4) cornstalk and paper properties

Sample	Cook time (min)	Screened yield(%) of initial cornstalk	Kappa No	CSF (mL)	ISO-brightness (%)	Scatt. Coeff. (m^2/kg)	Tensile index, (N·m/g)	TEA (J/m^2)	Burst index, (kPa·m^2/g)	Tearing index (mN·m^2/g)
CSP-4	60	44	32.8	600	23.5	23.1	98	97	4.9	6.1
CSP-6	30	38.7	9.2	600	39.5	21.3	97	90	5.0	6.1
CSP-7	15	41.6	6.5	550	39.4	20.5	106	108	5.72	6.4
CSP-8	30	41.7	5.9	552	39.1	21.2	104	103	5.8	6.0

For comparison purposes, cornstalk without prior hydrolysis was pulped using soda-AQ process and paper properties are presented in table 6. The washed solid residue after acid prehydrolysis was subject to pulping. The solid residues from hydrolysis experiment CS-23 was chosen based on sugar extraction and solid residual amount for pulping. The solid residues were pulped under various cooking conditions. The Canadian standard freeness of the pulp samples from different pulping conditions varied from 500 mL to 600 mL. The pulps were not refined further before handsheet making. The pulp yield (screened) based on initial cornstalk (OD) is around 41.5% except sample CSP-6 where AQ was not used in pulping. Yield is only 38.7% without AQ. AQ gives some protection against cellulose/hemicellulose degradation in pulping process. A 3% pulp yield gain (the difference CSP-6 and CSP-8) was a result of the presence of AQ in the pulping liquor in CSP-8. The screen reject was around 1.5% in cornstalk pulp, while reject was less than 1% for hydrolyzed solid residues pulp. The pulping of hydrolyzed solid residue required far less drastic condition (pulping temperature and duration) or low H-factor to yield comparable and/or better pulp than that directly derived from cornstalk. Although the pulp yield of direct cornstalk is 44% slightly higher than the yield of hydrolyzed solid residues of 41.5%, the kappa number is 32.8 much higher than 6 to 7 for the later. One would expect the pulp yield for direct cornstalk pulping to drop significantly, below the yield of prehydrolyzed solid residuals, to reach a final pulp kappa number of around 6~7. The brightness of the pulps derived from prehydrolysis run is almost 70% higher than the pulp from *direct pulping of cornstalk* under the same alkalinity.

Light scattering coefficient is a measure of the degree of bonding in paper and generally inversely proportional to paper strength properties. The scattering coefficient of the handsheet from direct pulping cornstalk is higher than those from hydrolyzed cornstalk solid residues, suggesting poor bonding The prehydrolysis runs (except the CSP-6 that was cooked without AQ) also produced paper with equivalent tear strength and higher tensile energy absorption (TEA), tensile index, and burst index than the direct pulping run. The results in Table 5 also demonstrate the importance of having hemicelluloses in the pulp. Sample CSP-6, where hemicellulose protector was not used, showed lower tensile and burst strength than CSP-8, in which AQ was used. The paper properties in Table 5 clearly demonstrate the feasibility of prior separation of certain fraction of carbohydrates in the form of fermentable sugar without affecting the paper making quality of cornstalk.

CONCLUSION

Cornstalk that contains high hemicelluloses and low lignin compare to wood is a potential source of energy and papermaking fiber. It is possible to extract 10 to 15% of the total carbohydrate in cornstalk through dilute acid hydrolysis prior to pulping without affect paper properties. Moreover, pulping process will require a lower cooking temperature and short cooking time (or lower H-factor) than direct pulping of cornstalk. Pulp produced from hydrolyzed cornstalk shows higher brightness, lower kappa number, and higher paper strength properties than the pulp from direct pulping of cornstalk.

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