Removal of Residual Lignin of Ethanol-Based Organosolv Pulp by an Alkali Extraction Process

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ABSTRACT: Organosolv pulps usually have high kappa number. This research investigated an alkaline extraction method prior to bleaching for reducing the kappa number of organosolv pulp. Ethanol wheat straw pulp with a kappa number of 58.2 was extracted with 1% NaOH solution. The results show that the ethanol pulp has a large amount of lignin particles on the fiber surface. After 1 min alkali extraction, the kappa number of the ethanol pulp is reduced by 60%, to 22.2, and both the number and the size of the lignin particles on the fiber surface are significantly reduced. In comparison with a further ethanol washing/extraction, the alkali extraction is much more effective in terms of lignin removal. X-ray photoelectron spectroscopy results show that a thin layer of lignin remained on the fiber surface after alkli extraction, but this did not reduce the internal bond strength. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 630–636, 2007

Key words: organosolv pulping; ethanol wheat straw pulp; lignin removal; alkali extraction; surface lignin; ESCA/XPS; SEM; biomaterials; surfaces; renewable resources; fibers

INTRODUCTION

Cellulose and lignin are the two most abundant natural polymers on the earth. How to efficiently use them has been a perpetual research topic. The emerging biorefinery concepts and research activities are good examples. A large portion of the lignocellulose materials such as wood and certain annual plants have traditionally been used to make pulp for producing paper. In a typical Kraft pulping process, lignin is removed from wood and then is burned to generate energy which is needed in the pulping and papermaking process, and cellulosic fibers are extracted to make paper. An alternative to Kraft pulping technology is a so-called organosolv pulping which uses organic solvents such as ethanol to remove lignin from wood. A substantial amount of research work has been conducted on organosolv pulping. This is mainly driven by the environmental impact and highly intensive capital cost occurring from the Kraft pulping system. It has been reported that organosolv pulp is particularly suitable for hardwood species and annual plants.[1–4]

The positive research results led to the building of the first North American pilot plant demonstration in Repap Enterprises in New Brunswick, Canada.[1,5] Organosolv pulping produces pulp with high yield and easier bleachability than conventional Kraft pulp and with comparable pulp properties. The economic scale of the organosolv pulping mill can be much smaller than a Kraft pulp mill. Since annual plants are bulky, the transport cost would be high if the capacity of a mill is large. This is particularly important for mills using annual plants as raw material. As wood supply is decreasing in many parts of the world, the use of annual plant fibers has drawn renewed attention from the pulp and paper industry in recent years. On the other hand, in Western Canada and Northwest America, disposal and open field burning of agriculture residues have been banned by air pollution control laws. Use of annual plants as an alternative fiber raw material for papermaking may be an effective way to reduce the environmental impact and at the same time to obtain economic benefits.

One of the distinct features of the ethanol pulp is that even with high kappa number which is a measure of lignin content of pulp, the pulp is easy to bleach. Lora and Aziz reported[6] that ethanol aspen pulp of a kappa number 30 was bleached to 81–86% ISO brightness with a simple chlorine bleaching sequence (CEH) and to about 90% ISO brightness with a chlorine dioxide bleaching (DED) bleaching sequence. Ethanol birch pulp of a kappa number 40 was bleached to 83% ISO brightness with a CEH

bleaching sequence. Cranland and Powers[7] reported that hardwood organosolv pulp could be delignified more extensively in the oxygen delignification stage than corresponding Kraft pulp. Delignification up to 75% was achieved without significant reduction of pulp viscosity, and pulp was bleached to a brightness level greater than 92% ISO after either an elemental chlorine free (ECF) sequence or a totally chlorine free (TCF) sequence. In comparison, delignification level of Kraft pulp in oxygen delignification is usually limited to below 50% to avoid the cellulose degradation. Lora and Pye[2] also found that ethanol wheat straw pulp was very receptive to alkaline extraction and to alkaline oxygen delignification.

However, the question remains why organosolv pulp has better bleachability. According to Nikhil and Paszner,[8] delignification takes place preferentially in the middle lamella region of fibers in the organnosolv pulping rather than in the secondary wall region as in the Kraft pulping process.[9] Therefore, fiber separation occurs earlier with regard to delignification level than in the Kraft pulping process. This explains the reason that organosolv pulp has high kappa number; however, it does not explain why the high kappa number pulp is receptive to bleaching. In a previous study,[10] it was found that a large number of lignin particles were precipitated on the surface of both eucalyptus pulp fibers and wheat straw pulp fibers in the ethanol pulping and washing process. The precipitation of the dissolved lignin on the fiber surface from the spent liquor was mainly due to the decrease of ethanol concentration in the washing liquor or the decrease of temperature. By increasing the number of the ethanol washing stages, the amount of lignin particles and the average size of the lignin particles on the fiber surface were reduced.

If the majority of the residual lignin in organosolv pulp is from the precipitation of the dissolved lignin from the spent liquor, it may explain the easy bleachability of the pulp. Since dissolved lignin has a lower molecular weight and less crosslinked structures, it is more reactive toward bleaching chemicals.[6,11,12] Moreover, precipitated lignin may not have a strong binding with fibers, so some of it may be simply removed by a washing mechanism. The objective of the present work is to investigate whether the residual lignin of the ethanol pulp can be removed by an alkaline extraction process. Reduction of residual lignin prior to bleaching with such a process can reduce the amount of bleaching chemicals required and thus reduce the environmental impact of the bleaching process.

EXPERIMENTAL

Ethanol pulping and washing

Wheat straw from a mill in Shaanxi, China, was pulped in a one-liter stainless steel tube reactor.

TABLE I
Ethanol Pulping and Washing Conditions

	Wheat straw
Cooking conditions	
Ethanol/water	55% (v/v)
Solid/liquid	1 : 8
Cooking temperature	195°C
Time to temperature	< 30min
Time at temperature	120min
Washing conditions	
Ethanol/water	55% (v/v)
Liquor/pulp ratio	12 (mL/g)
Washing temperature	145°C
Washing time	30 min

Ethanol–water solution and the raw material were packed into the reactor at a certain solid–liquid ratio. An oil bath was used to heat it to the required temperature for the cooking and washing experiment. After cooking, the reactor was cooled down with tap water and the pulp was removed into a Buchner funnel to filter the spent liquor from the pulp. Washing of the pulp was carried out for two stages with each stage being performed in the same reactor with the same ethanol–water solution as used in the cooking but at a lower temperature. After each washing stage, the reactor was cooled down by tap water and the pulp was removed into a Buchner funnel for washing with water. Pulp samples were collected for further analysis. Detailed pulping and washing conditions are listed in Table I. Lignin content of pulp samples was measured with Kappa number method according to TAPPI standard (T236).

Pulp extraction with 1% NaOH solution

Three grams (o.d.) of ethanol wheat straw pulp of a consistency of 20% was weighed into a 300 mL beaker, and then put in a water bath to heat to 100°C. Hundred milli liter of 1% NaOH solution in a 250-mL beaker was also heated in the same water bath. Once the pulp and the NaOH solution were heated to about 100°C, the NaOH solution was mixed with the pulp in the 300 mL beaker, and the mixture was agitated by hand with a glass bar and timing was started at the same time. The concentration of NaOH in the mixture was in the range of 0.9–1.1%, taking into account the moisture in the pulp. The pulp was extracted with NaOH for 1 min, 5 min, 15 min, and 60 min, respectively. After extraction, the pulp was removed into a Buchner funnel to filter the spent liquor and then washed with deionized water to neutral pH. The pulp was collected for further analysis.

Microscopic analysis

Fibers were imaged using a Leica light microscopy (DM4000M) in transmission mode. Prior to imaging,

pulp fibers were stained with Herzberg reagent to label lignin according to TAPPI standard method, T401om-93.[13]

SEM images of pulp fibers were obtained using a JEOL JSM-6400 scanning electron microscope, operated in secondary electron mode at an accelerating voltage of 10 kv. Prior to imaging, fiber samples were coated with gold for 120 s using a S150 sputter coater.

X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) was performed on a Leybold Max200 X-ray photoelectron spectrometer. Samples were mounted on a sample holder and the analysis was performed under a vacuum less than 10^{-9} torr. The analyzed area was 1 × 7 mm^2. Monochromated Al K(sources were used and operated under 12 or 15 kV and at 15–25 mA. The XPS spectra were obtained with a photoelectron take-off angle of 90° relative to the sample surface. For fiber samples, a charge compensation device was used to neutralize the charge buildup on the samples due to electron emission. The energy scale of the spectrometer was calibrated to Ag $3d_{5/2}$ peak at 368.3 eV and Cu $2p_{3/2}$ peak at 932.7 eV.

Atomic ratios of oxygen to carbon (O/C) were obtained by operating in a low-resolution mode with pass energy of 192 eV. The sensitivity factors for carbon and oxygen were 0.32 and 0.75, respectively. The carbon spectrum was also obtained by operating in a high resolution mode with a pass energy of 48 eV.

Fiber samples were prepared in sheet form. The sample sheets were placed on a clean metal plate, pressed lightly, and then dried at room temperature. The smooth side of the sample was used for XPS measurement.

Internal bond analysis

The internal bond strength (IBS) of hand sheets was tested with a Monitor/Internal Bond Test Station manufactured by IMI Test Machine Inc. Handsheets for the testing were prepared with a nominal basis weight of 80 g/m^2 on a British Standard Sheet Machine and then pressed and dried according to TAPPI standard method T205om-88.[13] Samples were conditioned at 50% RH and 23°C for at least 24 h prior to testing.

RESULTS AND DISCUSSION

Residual lignin on the ethanol pulp surface

In a previous study,[10] it was found that a large number of lignin particles is present on the fibers of both
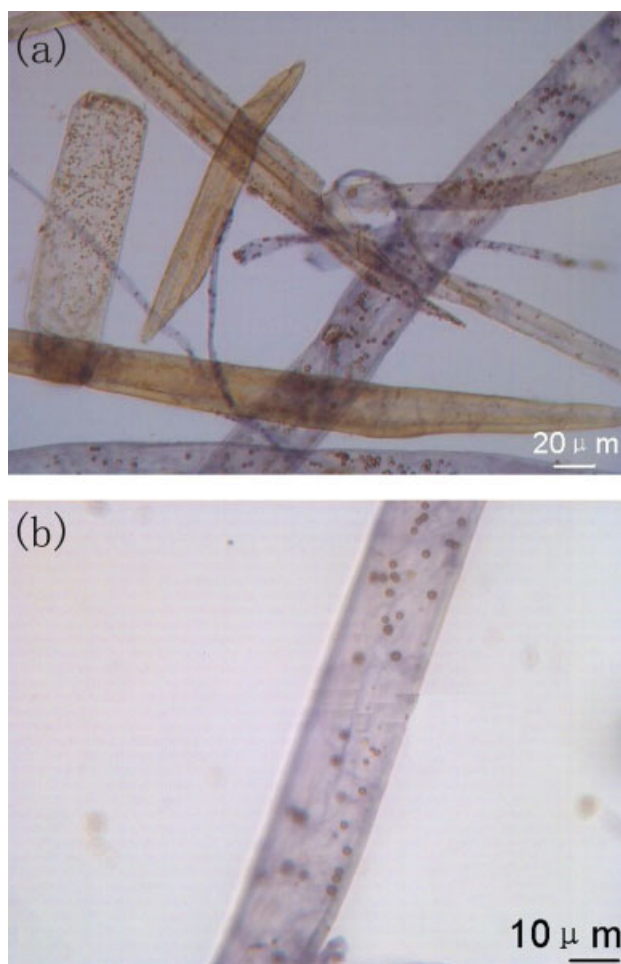

Figure 1 Light microscopic images of ethanol wheat straw pulp fibers, (a) after cooking, kappa 94.0, and (b) after a two-stage ethanol washing, kappa 58.5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ethanol eucalyptus and ethanol wheat straw pulp after ethanol pulping and after each stage of ethanol washing or ethanol extraction. Figure 1(a) shows fibers of ethanol wheat straw pulp after cooking without any washing. It can be seen that various sizes of lignin particles are present not only on the fiber cells but also on the vessel cells and parenchyma cells. After a two-stage washing with the same ethanol aqueous solution as used in cooking, i.e., 55% ethanol (v/v), the number of lignin particles on the fibers is still large as seen in Figure 1(b). According to Xu et al.,[10] the lignin particles are mainly from the precipitation of the dissolved lignin in the spent liquor onto the pulp fibers. Therefore, the residual lignin is expected to have similar characteristics as the organosolv lignin. It has been reported[6,11,12] that organosolv lignin has a lower average molecular weight and is more reactive than Kraft lignin and lignosulphonate. Lora et al.[11] also found that organosolv lignin has a low solubility in
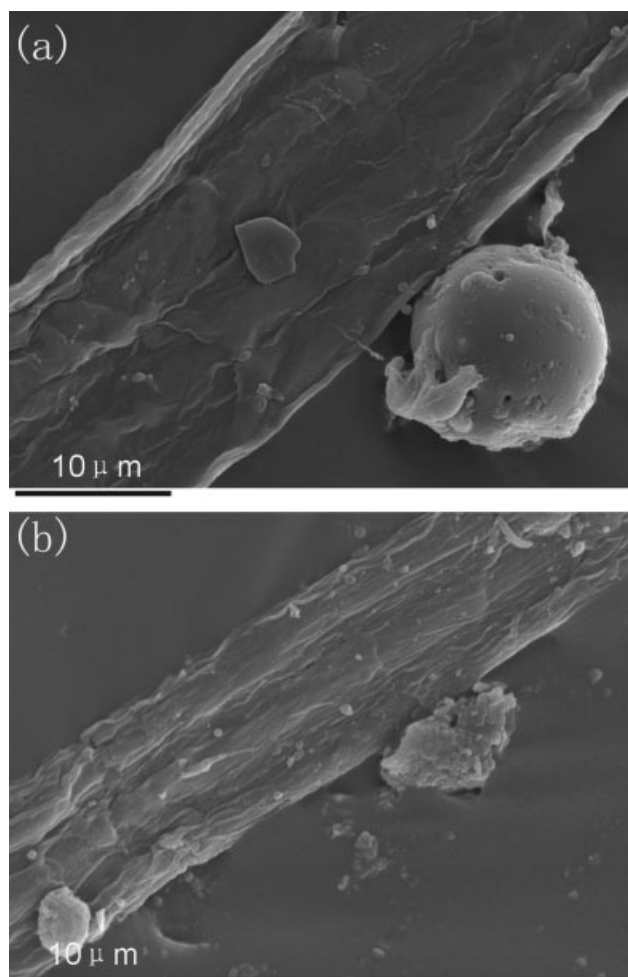
Figure 2 SEM images of ethanol wheat straw pulp fibers, (a) after a one-stage ethanol washing, kappa 76.0, and (b) after a three-stage ethanol washing, kappa 60.3.

water and neutral or acid solutions but is soluble in dilute alkaline solutions. In addition, in the present experiment, it was found that in preparing pulp slurry for handsheet making or for sampling fibers for microscopic observation, some lignin particles could be washed off the fibers in the process of the mechanical disintegration of the pulp slurry. It can be seen from Figure 2(a) that a big lignin particle is washed off the fiber, and from Figure 2(b) that a big lignin particle and many small lignin particles are washed off the fiber. It should be noted that the fiber samples for SEM observation were prepared by putting a drop of the pulp slurry on the sample holding disc and letting it dry in air, so the lignin particles in the liquid phase of the pulp slurry were retained on the sample holding disc after drying. Therefore, it was expected that a washing process with a dilute alkaline solution would remove part of the residual lignin from the organosolv pulp by both the dissolving power of the alkaline solution and the agitation action in the washing process.

Removal of residual lignin by alkaline extraction

Ethanol wheat straw pulp after a two-stage ethanol washing process was used as the starting pulp for alkaline extraction since ethanol pulping of straw usually uses a one-stage cooking with a two-stage extraction. This pulp has a kappa number of 58.5 and still has lignin particles on the fiber surface as shown in Figure 3. Alkaline extraction was conducted with 1% NaOH solution for 1 min, 5 min, 15 min, and 60 min, respectively. It can be seen from Figure 4 that kappa number decreases dramatically, from 58.5 to 22.2, by more than 60%, after the first 1 min alkaline extraction. Further prolonging the extraction time reduces kappa number but at a much slower rate. This indicates that about 60% of the lignin in the ethanol pulp is soluble in 1% NaOH solution, and it may be from the precipitation of the dissolved lignin on the fibers in the previous cooking and washing process. The rest of the lignin in the pulp is difficult to remove by alkali extraction, similar to the residual lignin in Kraft pulp which has large molecule size or is associated with the lignin-carbohydrate compounds. It can be seen from Figure 5 that the lignin particles on the fiber surface are in general reduced after extraction compared with the original pulp fibers as shown in Figure 3, but they are still apparently seen. Nevertheless, the kappa number decreased by more than 60% after alkaline extraction for only 1 min, which shows that the extraction process is an effective way to remove residual lignin in ethanol pulp. It is known that a common feature of the organosolv pulp is its high kappa number. If the pulp is sent to the bleaching stage directly, high bleaching chemical charge would be required, and more toxic substances may be generated in the bleaching effluents, in particular, in the chlorine or DED process.
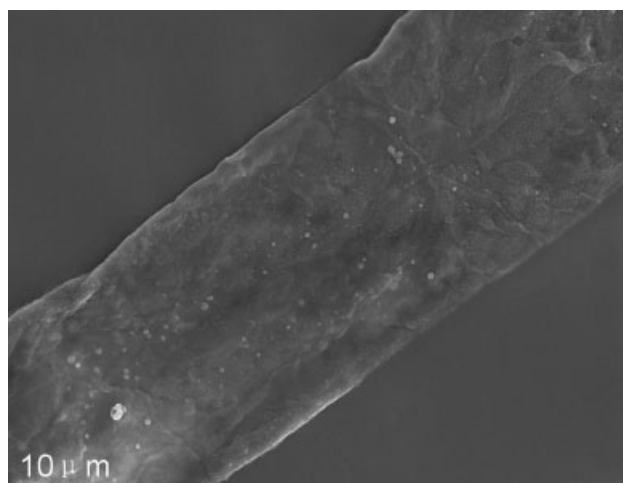

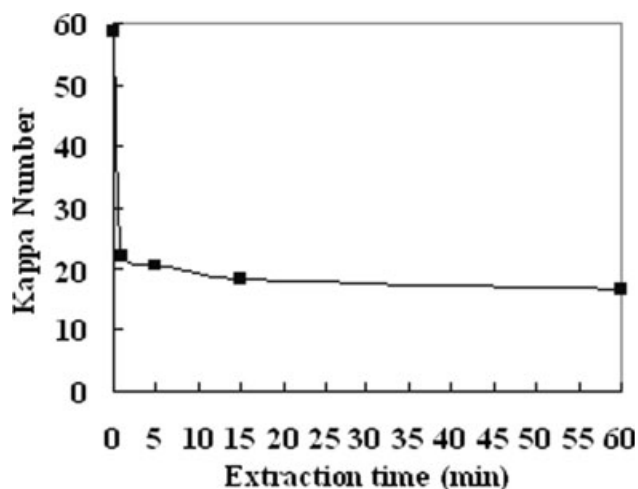**Figure 3** SEM image of the ethanol wheat straw pulp of after a two-stage ethanol washing, kappa 58.5.

Figure 4 The kappa number of ethanol wheat straw pulp versus 1% NaOH extraction time.

According to our previous study,[10] after two more stages of ethanol washing, i.e., four stages of washing in total, kappa number of the same ethanol wheat straw pulp was decreased by only about 15%, from 58.5 to 49.8. Compared with the ethanol washing, alkaline extraction is much more effective in terms of removing lignin.

Effect of alkaline extraction on the fiber surface lignin

XPS has been used in several studies[14–18] to determine the surface lignin of pulp fibers. Li and Reeve[14,15] proposed a systematic methodology to determine surface lignin concentration. This methodology requires a great deal of experimental work, and the exact lignin molecular structure needs to be known. On the other hand, comparison of lignin concentration of the same pulp can be obtained by the atomic oxygen to carbon ratios of the samples determined by XPS. The theoretical O/C ratios of cellulose and lignin are 0.83 and 0.33, respectively. Therefore, higher O/C ratio indicates lower lignin concentration. Furthermore, surface lignin concentration can be interpreted by the carbon to carbon only bonds determined by XPS. According to Dorris and Gray,[16] high resolution carbon spectrum can be
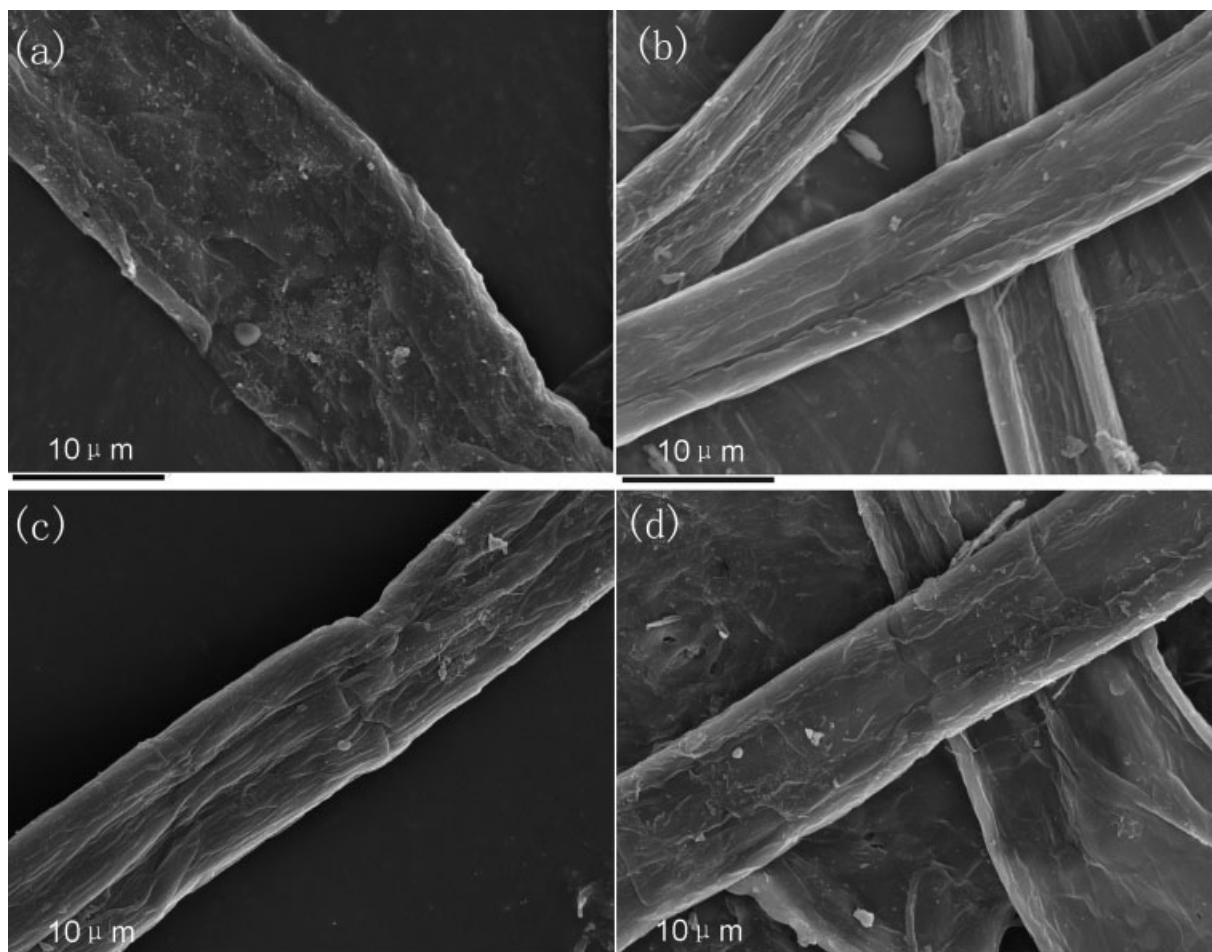

Figure 5 SEM image of ethanol wheat pulp fibers extracted by 1% NaOH for (a) 1 min, (b) 5 min, (c) 15 min, and (d) 60 min.

TABLE II
Atomic O/C Ratios and Carbon Peak Deconvolution
of the Ethanol Wheat Straw Pulp Extracted
with 1% NaOH Solution

Extraction time (min)	O/C ratios	C1 (%)	C2 (%)	C3 (%)	C4 (%)
0	0.46	33.9	48.6	15.8	1.7
1	0.45	41.0	43.4	12.9	2.6
5	0.47	42.4	44.6	11.4	1.6
15	0.43	44.7	41.9	11.2	2.2
60	0.45	43.2	43.1	11.7	2.0

deconvoluted into different carbon components, i.e., carbon with different chemical environments. The types of chemical bonds of carbon in cellulose, hemicellulose, and lignin can be categorized into four groups:

C1: carbon atoms bonded only to carbon or hydrogen, i.e., C—C or C—H
C2: carbon atoms bonded to a single oxygen excluding a carbonyl oxygen, i.e., C—O in alcohols and phenols
C3: carbon atoms bonded to two noncarbonyl oxygen atoms or a single carbonyl carbon, i.e., O—C—O or C=O
C4: carbon atoms bonded to a single noncarbonyl carbon and a carbonyl carbon, i.e., O—C=O in carboxylic acids

C1 exists only in lignin, but not in cellulose and hemicellulose. Therefore, by determining the percentage of C1 of samples, surface lignin concentration can be compared.

Table II lists the XPS results of the pulps. It can be seen that the O/C ratio is decreased after the alkaline extractions with a major decrease occurring in the first 1 min extraction. The results are somewhat unexpected since lowered O/C ratio means increased surface lignin concentration. The same conclusion can be drawn from the C1 percentage. It can be seen from both Figure 6 and Table II that C1 percentage increases with alkaline extraction, and the major increase occurred in the first 1 min extraction, corresponding to the change of O/C ratio with the same extraction time. This means that the decrease of O/C ratio is due to the increase of C1 percentage, and due in turn to the increase of lignin concentration on the fiber surface. Since a substantial amount of residual lignin was removed from alkaline extraction, as reflected in the kappa number change, it is reasonable to expect that fiber surface lignin also decreases with the extraction. In addition, as observed in the foregoing SEM images, the lignin particles on the fiber surface were reduced both in number and in size. However, it should be noted that XPS only detects a surface layer about 10 nm

thick, so the surface lignin concentration determined by XPS is the lignin concentration in the 10 nm thick surface layer. For instance, if a lignin globule of a 500 nm diameter is present on a fiber surface, only the top 10 nm thick layer of the lignin particle will then contribute to the surface lignin concentration determined with XPS. Therefore, the present XPS results may reflect the true situation of the fiber surface. Since more than 60% of the residual lignin was dissolved by alkaline extraction, presumably from both the fiber and the inside fiber wall, the lignin concentration in the liquid phase would be high during the extraction. In this case, the dissolved lignin may adsorb on the fiber surface as small molecules as observed in Kraft pulping.[19–22] If this is the case, XPS can detect the change of the surface lignin concentration due to lignin adsorption, but SEM cannot, because of the resolution limit. This may explain the seeming discrepancy in the SEM and XPS results. On the other hand, XPS analysis shows that after alkaline extraction, although the kappa number of ethanol wheat straw pulp decreases dramatically, lignin is still enriched on the fiber surface. If present on the fiber surface, lignin will react with and dissolve more easily in the bleaching solution. This is in agreement with the result of Cronlund and Powers,[7] in that they found that alkaline extracted or oxygen-delignified ethanol pulp has a good response to subsequent bleaching such as ECF or TCF.
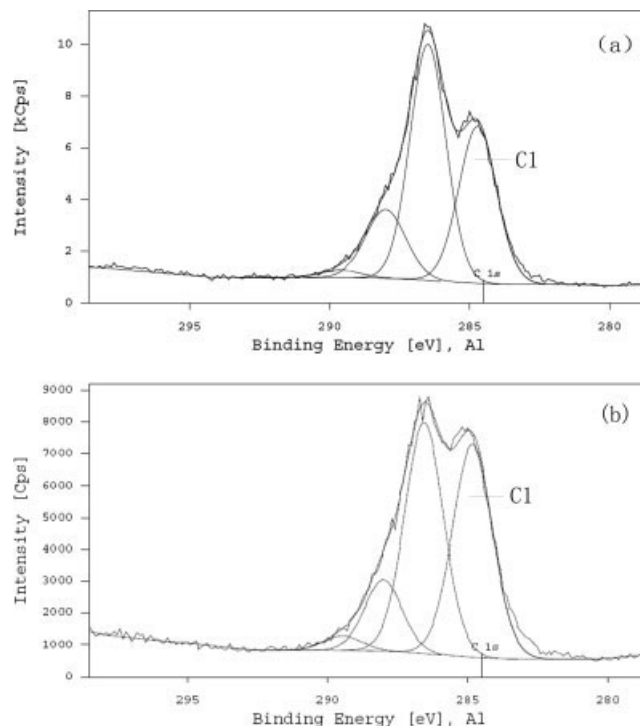

Figure 6 High-resolution XPS spectra of ethanol wheat straw pulp before alkali extraction (a) and after 1% NaOH extraction for 1 min (b).
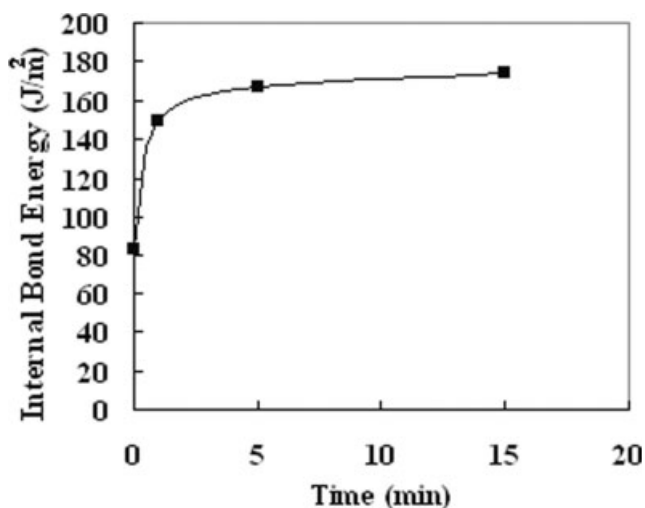
Figure 7 Handsheet internal bond strength versus alkali extraction time.

Effect of alkaline extraction on the interfiber bonding

As is known that alkaline condition facilitates fiber swelling, which benefits interfiber bonding because of increased bonded area. However, increased surface lignin concentration may impair interfiber hydrogen bonding.[23] Therefore, the IBS of the ethanol pulps was measured to evaluate the effect of alkaline extraction. It can be seen from Figure 7 that the IBS of the pulp almost doubled after the first 1 min extraction. This means that although increased surface lignin might affect negatively on the interfiber bonding, the positive effect of the alkaline extraction dominated. In fact, about 60% of residual lignin was removed by the alkaline extraction, including removal of the residual lignin inside the fiber wall and reduction of both the number and the size of the lignin particles on the fiber surface, which are both favorable factors for the interfiber bonding.

CONCLUSIONS

Wheat straw pulp has a very high kappa number of about 60 after one-stage ethanol cooking and two subsequent stages of ethanol washing/extraction. A large amount of lignin particles is present on the fiber surface, which can be observed by both conventional light microscope and scanning electron microscope.

Extraction of the ethanol wheat straw pulp with 1% NaOH solution for 1 min reduced kappa number from 58.2 to 22.2, which is more than 60% reduction. The lignin particles on the fiber surface are also reduced in both number and size. However, a small number of lignin particles are still seen on the fiber surface after alkaline extraction for 60 min.

XPS results show that although the kappa number is decreased substantially, the surface lignin concentration is increased with alkaline extraction. This is due to the adsorption of the dissolved lignin back on the fiber surface, similar to what is observed in Kraft pulping. However, the IBS increased with the extraction, which is attributed to the overall reduction of the residual lignin and the swelling of fibers by alkaline solution.

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